

ABSTRACT

of the dissertation for the degree of Doctor of Philosophy (PhD) in the specialty
6D060400 - "Physics"

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Structural-phase states and properties of detonation coatings based on titanium carbosilicide before and after pulsed plasma treatment

At the present time it is necessary to have low-cost, but highly effective technologies of surface modification and applying of protective coatings, allowing to increase the operational characteristics of steel products. Knowledge of the regularities of diffusion processes and the study of the kinetics of transformations that occur when applying coatings will significantly increase the efficiency of the search for optimal methods of their treatment. Currently the most effective is considered the use of high-speed coating spraying technologies, which are characterized by high productivity, universality and simplicity in control of technological parameters. Also, methods of product surface treatment using combined technologies, which stimulate the process of changing the structural-phase state of the material, thereby obtaining a modified surface layer or coating with the desired properties, are intensively developing.

Special interest is the production of composite coatings based on MAX-phase (ternary carbides $M_{n+1}AC_n$ and nitrides $M_{n+1}AN_n$, M - transition metal, A - element of IIIA or IVA subgroups). Interest in MAX phases (e.g. titanium carbosilicide Ti_3SiC_2) is due to its unique combination of the properties of metal and ceramics: as ceramics it is hard, low weight, high strength and wear resistance, has a high melting point and can be easily processed like metals. Among the newest composite materials is the family of so-called MAX compounds, which are carbides and silicides corresponding to the formula Ti_3SiC_2 . Due to the peculiarities of the crystal lattice structure, Ti_3SiC_2 is characterized by a unique combination of physical, chemical and mechanical properties. Also Ti-Si-C systems have good performance in abrasive wear, corrosion, as well as relatively low cost. The combination of high wear and corrosion resistance allows this material to be used as wear-resistant coatings. However, despite the uniqueness of the properties useful in practical terms, both solid materials and coatings made of Ti_3SiC_2 have not yet found widespread use in production. One of the limiting factors for the widespread use of Ti_3SiC_2 coatings is the difficulty in obtaining it as a single-phase product due to the decomposition of the MAX phases at the high temperatures of coating application. Obtaining coatings based on Ti_3SiC_2 by gas-thermal methods is usually accompanied by the formation of Ti-C and Ti-Si phases. Coatings with relatively high Ti_3SiC_2 content can be obtained by some thermal spraying methods, in particular by detonation spraying, which is carried out by using a gas explosion to accelerate and heat up the particles of the powder material being sprayed. In detonation spraying the powder material melts and moves at high velocity under the influence of the impact wave to the substrate forming a coating on its surface. Since the formation of structural-phase states of detonation coatings strongly depends on the technological mode of spraying, it is possible to increase the volume fraction of

the Ti_3SiC_2 phase by selecting the optimal spraying modes. Increasing the volume fraction of the Ti_3SiC_2 phase provides high mechanical and tribological properties of the composites.

The Ti_3SiC_2 content can be increased to some extent by volume or surface heat treatment. However, volumetric heat treatment has disadvantages associated with the substrate material unstrengthening, and the application of volumetric heat treatment is not economically feasible. Therefore, in our opinion, it is reasonable to apply the methods of surface heat treatment by concentrated energy flows. Surface heat treatment with concentrated energy flows can be performed by using a laser beam, electron beam, plasma flow, etc. Among them, of particular interest is the plasma heating source, in particular pulsed plasma treatment.

Thus, one of the prospective directions for obtaining single-phase Ti_3SiC_2 coatings with high tribological characteristics is the use of a combined method involving detonation spraying of Ti_3SiC_2 powder and subsequent pulse-plasma treatment. Therefore, it is necessary to study the regularities of formation of the structure and properties of titanium carbosilicide-based coatings depending on the technological mode of detonation spraying, and to study the effect of heating on phase transformations in titanium carbosilicide-based coatings, and to study the effect of pulse-plasma treatment mode on structural-phase states and properties of titanium carbosilicide-based coatings.

In the literature there is no general opinion on the formation of the structure and properties of coatings based on titanium carbosilicide depending on the technological mode of detonation spraying. And there are no data in the literature on the effect of pulse-plasma treatment on the structural and phase transformations in the detonation coatings based on Ti-Si-C. In addition, the tribological characteristics of coatings based on titanium carbosilicide have been insufficiently studied.

Therefore, the study of the regularities of formation of structural-phase states and tribological properties of coatings based on titanium carbosilicide depending on the technological mode of detonation spraying and on subsequent thermal and pulse-plasma treatment is relevant.

The aim of the work is to study the peculiarities of formation of the structural-phase state and properties of coatings based on titanium carbosilicide during detonation spraying and subsequent thermal and pulse-plasma treatments.

To achieve the goal set in this work, it is necessary to solve the following **tasks**:

- to determine the effect of detonation spraying parameters (ratio and volume of barrel filling with acetylene-oxygen mixture, spraying distance) on the formation of the structural-phase state and mechanical-tribological properties of coatings based on titanium carbosilicide;
- to study the phase formation process of detonation coatings based on titanium carbosilicide during heat treatment;
- to study the features of the structural-phase state of the surface layers of detonation coatings based on titanium carbosilicide during pulse-plasma treatment;

– to evaluate the wear resistance and to analyze the effectiveness of the application of carbosilicide coatings obtained by detonation spraying with subsequent pulse-plasma treatment.

The main statements made for the defense:

1. Formation of structural-phase composition and properties of coatings based on titanium carbosilicide depending on technological parameters of detonation spraying. Obtaining coatings based on titanium carbosilicide during detonation spraying with the following parameters: volume of explosive mixture of oxygen-acetylene 60% with $O_2/C_2H_2=1.856$ ratio, spraying distance 50 mm, provides high hardness ($\sim 1000HV$) and wear resistance due to minimal decomposition of Ti_3SiC_2 phase (phase content 39 weight %). When the volume of filling the detonation barrel with explosive gas mixture increases up to 70 % due to the high-temperature shock wave, decomposition of Ti_3SiC_2 (MAX phase) occurs and its volume fraction in the composition of the coatings decreases to 29 wt.%.

2. Changes in the structure and properties of detonation coatings based on titanium carbosilicide as a function of heating temperature. As a result of heat treatment at 700-900 °C for 1 h in the coatings based on titanium carbosilicide the structure-phase transformation with a slight increase in the volume fraction of MAX-phase (Ti_3SiC_2) and alignment of the coatings microstructure is observed. Thermal treatment at 800 °C for 1 h leads to increase of microhardness and wear resistance of coatings approximately in 2.0-2.5 times in comparison with samples before annealing.

3. Features of structural-phase transformations of detonation coatings based on titanium carbosilicide during pulse-plasma treatment. After pulse-plasma treatment at the following modes: electrode W, frequency 1.2 Hz, pass rate 5 mm/s, number of passes 1, treatment distance 50 mm, the MAX-phase content in the detonation coatings increases approximately 1.7 times. Processing of coatings by pulsed plasma flows allows to form a modified layer up to 20 microns thick. Modification of structural-phase state of near-surface layers of carbosilicide coatings leads to change of their mechanical characteristics: increase of surface microhardness up to 1.8 times, decrease of dry friction coefficient 1.5-2.0 times and increase of wear resistance of samples.

The object of the study is detonation coatings based on titanium carbosilicide before and after pulse-plasma treatment.

The subject of the study is the structural-phase transformations occurring in detonation coatings before and after pulse-plasma treatment and their relationship with the coating properties (hardness, adhesive strength, and wear resistance).

Methods of research. The structural and phase states of detonation coatings based on titanium carbosilicide were studied using the following experimental methods: X-ray diffraction analysis, scanning electron microscopy, transmission electron microscopy, electron Auger spectroscopy, and profilometry. Mechanical characteristics of the coatings were determined by scratch testing (scratch method), by measuring microhardness, as well as by measuring the hardness and modulus of elasticity of the coatings on the cross section of the sample by nanoindentation. Tribological properties of the coatings were determined by measuring the friction

coefficient and wear of rubbing surfaces according to the "ball-and-dick" scheme, as well as by abrasion and impact-abrasion tests.

During the work we used resources and equipment of Research Center "Surface Engineering and Tribology" and National Scientific Laboratory of Collective Use of Sarsen Amanzholov EGU, laboratory of Academician E.A. Buketov Karaganda University, Research and Production Company PlasmaScience LLP, Wrocław University of Science and Technology (Wrocław, Poland), Center for measuring the properties of materials of National Research Tomsk Polytechnic University (Tomsk, Russia) and the E.O. Paton Electric Welding Institute of the National Academy of Sciences of Ukraine (Kiev, Ukraine).

Scientific novelty of the work:

- for the first time the possibilities of application of detonation spraying for obtaining coatings based on titanium carbosilicide (Ti_3SiC_2), which provides a low degree of decomposition of MAX-phases, have been considered. Based on the evaluation of the influence of the main parameters of the detonation spraying mode on the structural-phase states and properties of the coatings a reasonable choice of the rational mode of coating deposition has been made;

- for the first time the influence of pulse-plasma treatment on the structural-phase states and properties (hardness and wear resistance) of detonation carbosilicide coatings has been studied. On the basis of the obtained data a new combined method of obtaining wear-resistant coatings including detonation spraying and subsequent treatment with pulse-plasma impact has been developed and its use as a finishing treatment for additional increase of mechanical and tribological characteristics of surface layers of coatings has been proposed. The developed method is protected by a patent for a useful model "Method of obtaining wear-resistant coating" (№ 6659 published on 12.11.2021).

Practical significance. Effective ways of increasing the wear resistance of detonation coatings based on titanium carbosilicide with the use of pulse-plasma treatment have been proposed. The results obtained can be used to improve the technology of obtaining wear-resistant coatings based on MAX-phase to improve the service life of steel parts, in particular parts of tillage machines, working in conditions of wear and friction.

Relationship of the work with research projects. Dissertation work on "Structure-phase states and properties of detonation coatings based on titanium carbosilicide before and after pulse-plasma treatment" corresponds to the priority direction of science development "Power engineering and machine building" and was performed in accordance with the following projects funded by the Scientific Committee of the MES RK:

- BR05236748 "Research and development of innovative technologies for obtaining wear-resistant materials for mechanical engineering products," program-targeted funding for 2018-2020, contract No. 197 of 16.03.2018;

- AR08957719 "Development of method of hardening and restoration of working elements of tillage machines", grant financing for 2020-2021, agreement №223 from 12.11.2020.

Author's personal contribution. The author's personal contribution consists in participation in conducting experiments, obtaining the results presented in the dissertation, generalizing and analyzing the results obtained, and writing scientific articles on the topic of the dissertation. Statement of the problem, formulation of the main conclusions and provisions of the dissertation work were carried out jointly with scientific advisors.

The degree of validity and reliability of the results is provided by the use of modern methods for studying the structure, chemical and phase composition, surface profile, mechanical and tribological tests, standard test procedures, large volumes and repeatability of experimental data. The results of the research carried out in the dissertation work do not contradict the known scientific notions and results.

Approbation of the work results. The main results were presented at: The 11th International Symposium "Powder metallurgy: surface engineering, new powder composite materials. Welding", Minsk, Belarus, April 10-12, 2019; in the International Scientific and Practical Conference "XXXVIIIth Autumn Tribology School 2019" from 10 to 13 September 2019. ; XIII International Scientific and Practical Conference "International Trends in Science and Technology", Warsaw, Poland, May 25, 2019; VI International Conference "Laser, Plasma Research and Technology - LaPlaz-2020" February 11-14, 2020; 14th International Symposium "Powder Metallurgy: Surface Engineering, New Powder Composite Materials. Welding", Minsk, Belarus, September 9-11, 2020; IEEE 10th International Conference on "Nanomaterials: Applications & Properties" (NAP-2020) Sumy, Ukraine, November 9-13, 2020; IEEE 11th International Conference Nanomaterials: Applications & Properties (NAP-2021) September 5-11, 2021; in the International Conference "Physical Mesomechanics. Materials with Multilevel Hierarchically Organized Structure and Intelligent Manufacturing Technologies", Tomsk, 2021. In addition, the main scientific results were reported and discussed at the scientific seminars of the Department of "Physics and Technology" and the research center "Surface Engineering and Tribology" of Sarsen Amanzholov EKV.

Publications. There were published 19 works on the dissertation theme, including 5 articles in the peer-reviewed scientific journals indexed in the Web of Science and Scopus databases, 4 articles in the journals recommended by the Committee on Quality Assurance in Education and Science of the MES RK, 9 works in the proceedings of national and international conferences, and 1 patent for a utility model of the Republic of Kazakhstan.

Structure and volume of the thesis. The thesis consists of an introduction, five chapters, a conclusion, a list of 224 references, and 2 appendix. The total volume of the dissertation is 113 pages, including 64 figures and 16 tables.