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"Scientific and Production Association "Geoenergetica"

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Investigation of mechanical properties and structure structural materials, modified ultradispersed particles of minerals

RESUME OF DISSERTATION

for the academic degree Philosophy Doctor Higher School of Economics

(PhD HSE)

Engineering and Applied Mathematics

Scientific adviser:

Doctor of Physical and Mathematical Sciences,

Professor

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Moscow – 2018

The actuality of the research and the statement of the problem

The actuality of the investigation consists in the presence of a problem of increased wear of friction pair parts operating in an aggressive environment: abrasives of various origins, thermocyclic loads in a wide range of temperatures, hydrogen sulfide and other gases, sea water, acid solutions.

Under these conditions, the wear and corrosion damage of the surface layers of friction units of machines and mechanisms increases sharply, which leads to considerable expenses for repair and production of spare parts. Conventional structural materials, providing a general strength of the structure, often do not meet the requirements of high wear resistance and corrosion resistance. To eliminate and / or inhibit processes occurring at the metal-environment boundary and adversely affecting the performance of materials, various types of surface treatment are used.

Such methods of increasing the hardness of metal parts as nitriding, carburizing, other surface modification methods, as well as methods for creating coatings, protective films and layers by galvanic methods, methods of heat treatment, ion-plasma treatment, microarc oxidation, gas-plasma spraying and others. Only methods of modifying the surface to date, several hundred are known. Each of the methods of surface treatment has its advantages and disadvantages, as well as limitations in the application. The merits of many of these methods include relatively low cost, high speed of coating, disadvantages - adhesion problems, the appearance of defects, restrictions imposed by the size of baths, ovens, evacuated space, changing the geometry of the part after processing.

The shortcomings of many methods can also be attributed to low economic efficiency, since often the processes of creating layers or coatings are accompanied by long-term high-temperature heating, limiting the mass-size dimensions, and the fragility of the layers obtained. High temperatures can lead to a change in the structure of the metal, a reduction in strength properties, leashes and a low yield.

Therefore, it is actual to develop other methods for modifying a metal surface with minimal or low thermal impact.

One of the effective technologies for creating protective layers on the details of friction pairs, in the operation of which showed good results, is the technology of mineral coatings. The essence of the technology lies in the creation of a modified surface layer, usually 5-30 μm thick, by its plastic deformation by means of ultrasonic and mechanical influences, which activate the occurrence of ultradispersed particles of minerals in the metal volume, as well as processes, while protected in know-how mode.

Applied research on the development of technology of mineral coatings and the results of its application at different times were conducted in the following areas: studies of the properties of mineral materials; research of the properties of coatings from mineral materials and the technology of their formation; research of parameters and characteristics of parts, assemblies and mechanisms with mineral coatings.

Currently, about 80 types of mineral materials are used to create multifunctional mineral coatings. The fundamental basis of applied research on the use of mineral materials for the creation of coatings are works on crystal chemistry and crystallography V.V. Zuev, Yu.V. Kholopov, S.Yu. Lazarev. The types of materials used are determined by the composition and amount of impurities, the structural-phase state of the constituent components and other characteristics. The classification of natural mineral materials used to enhance the parameters of parts, assemblies and mechanisms has not yet settled and is waiting for its researcher who has a systemic approach and who has access to information on the composition of mixtures.

Investigation of the properties of coatings from mineral materials and the technology of their formation have been initiated since the creation of the basic

process steps of the technology of mineral coatings. Most of the works are devoted to applied research of properties and parameters of coatings of specific parts and mechanisms, in particular, turbine control units for geothermal stations, bearings, water lubrication, parts of internal combustion engines, parts of turbines, gears and others. The mechanisms of wear of concrete parts with mineral coatings, changes in the coefficient of friction of parts, the value of adhesion numbers of a number of materials with mineral coating, and the resistance of coatings in some corrosive environments were investigated.

Despite the existing reserve of scientific works on the study of the properties of parts exposed to the technology of mineral coatings, it turned out that the microstructure of the layer modified by the minerals was never investigated. Until recently, it was not known what the metal surface was as a result of the application of processes of mineral coating technology: this coating or a modified layer.

It should also be noted that to the experimental data published in many articles, there are many questions that remain unanswered due to the lack of important details, which leads to the fact that part of the experiments cannot be repeated and correctly interpreted, and also used in calculations. There is a problem of the correctness of the measurement of the physical and mechanical properties of thin coatings and thin modified layers, arising from the presence of factors that lead to methodological errors for some methods of measuring wear resistance, hardness, and modulus of elasticity. The most significant factors that introduce distortion when registering a response are the surface roughness, residual stresses and the effect of the substrate. One of the methods lacking some of the above drawbacks is the sclerometry method, which has not yet been used to measure surface parameters after modification by ultradispersed particles of minerals. Various physical models of a metal surface modified with mineral particles and the underlying causes underlying them can be checked, including on the basis of qualitative experimental data.

Such technology possibilities as the possibility of forming mineral layers on complex shape and configuration details, the possibility of surface modification at relatively low layering temperatures, without changing the geometric dimensions, have determined one more object for application - thread and thread connections of the clutch-nipple type from various types of steels, used in shipbuilding, oil and gas production, mechanical engineering, the tribotechnical parameters of which until recently remained unknown. The urgency of the investigation of the wear resistance of threaded joints with mineral coatings is evident for increasing the life of steel parts.

Another problem is changing the tribotechnical parameters for local and / or general heating, which can lead to intensification of destructive processes on the surface and in the volume of the part, which affects its wear resistance and life. Heating during operation and the subsequent acceleration of the wear process, for example, sliding and rolling bearings, reducers, worm gears and other parts is a typical case that occurs when operating various mechanisms and devices, especially large masses. Therefore, a decrease in the friction coefficient or its stabilization upon heating, a decrease in the temperature of rubbing metal surfaces is an actual task of material science for practically all industries. Determination of the temperature dependence of the coefficient of friction of a metal part allows in some cases to predict the resource of various details and can serve as a basic experiment in predicting the properties of various parts with mineral coatings in other cases.

The purpose and objectives of dissertation research

The aim of the work is to obtain new data on changes in the surface structure and near-surface layers, as well as the mechanical properties of a number of structural materials (low-carbon steels, titanium and aluminum alloys) modified by

ultradispersed mineral particles to develop effective methods for improving the tribological characteristics of materials and products from them in production conditions.

In the present work several actual practical problems were solved:

- obtaining new data on changes in the structure of the metal surface and near-surface layers of samples from ferritic-martensitic chromium steel and titanium alloy VT6 (Ti-Al-V) in the creation of mineral coatings;

- obtaining new data on the mechanical properties of the titanium alloy VT6 (Ti-Al-V), modified with ultradispersed particles of minerals, using the sclerometry method to minimize the influence of the substrate;

- obtaining new data on the temperature dependences of the coefficient of friction of specimens made of steel modified with ultradispersed particles of minerals, with different surface roughness;

- Improvement of tribological parameters of samples from low-carbon steel with mineral coating to determine the possibility of their use in the manufacture of stop valves;

- Improving the tribological characteristics of threaded joints of several types of steel pipes, after modification of their surface by particles of minerals, to determine the possibility of their use in the oil and gas sector.

The object of the dissertation research is structural metal materials (low-carbon steels, titanium and aluminum alloys), modified by ultradispersed particles of minerals.

The subject of the study are the mechanical properties and structure of metal alloys (low-carbon steels, titanium and aluminum alloys) modified with mineral particles.

Methodological basis of the research

Experimental data were obtained using modern, high-precision and metrologically certified equipment using standard methods and GOSTs.

Microphotographs of the surface structure of the samples were obtained with a Supra 40 scanning electron microscope equipped with an X-Flash EDRS detector and with the Quantax 4000 software.

The surface roughness was measured on a profilometer, model 130, the manufacturing enterprise PROTON MIET.

The hardness and modulus of elasticity were measured with a NanoScan-4D nanodidomer. The method of measurement is the indentation of a diamond pyramid with registration of an indentation diagram and subsequent calculation of hardness and elastic modulus in accordance with GOST 8.748-2011 (ISO 14577). The wear resistance was measured using a NanoScan-4D scanning hardness tester using the sapphire sphere multi-cycle friction method with the control of the clamping force and the tip deepening into the sample.

The method of determining the life of a threaded joint of tubing was to conduct multiple tests for screwing-unscrewing the lock of a tubing with the registration of torque at each stage of the test and the determination of the tightness with threaded calibers.

The measurement modes and details of the experiments are in the corresponding sections of the chapters of the dissertation.

Scientific novelty of dissertational research

1. As a result of structural studies of a number of structural materials, it has been established that the technology of mineral coatings does not create a coating as such, but creates a uniform modified layer, in the absence of a sharp coating boundary with the base metal.

2. New experimental data on a number of mechanical properties (wear resistance, modulus of elasticity, roughness) of a titanium alloy VT6 (Ti-Al-V) modified with ultradisperse particles of minerals were obtained using the sclerometry method.

3. For the first time, a study was made of the temperature dependence in the 30-140 °C range of the friction coefficients of samples from low-carbon steels 12X13 and 18X2N2M with mineral-modified layers. It was found that under the experimental conditions (contact pressure 550-600 MPa, displacement speed 4-74 mm /s, Mobil SHC 639 oil), the coefficient of friction remains practically constant for samples with mineral coatings (increases by no more than 10% of the coefficient of friction at room temperature), in contrast to the friction coefficient of unmodified samples, including hardened ones, for which its value increases by more than 50% for the same tests.

4. It has been established that the degree of wear of the toroid from alumina conjugated to disks of steel 12X13 with mineral coating when rotating in water is below the level of registration of the degree of wear and cannot be quantified in the experiment (water temperature T = 23 °C, linear velocity v = 0.1 m /s, the total travel distance s = 2 km). The value of the coefficient of volumetric wear of the alumina toroid, conjugated with mineral-coated discs when rotating in water, is at least two orders of magnitude smaller than the values of the coefficient of volume wear during rotation with uncoated discs.

5. The physical mechanism of the effect of a sharp increase in the wear resistance of metal alloys modified by ultradispersed particles of minerals is proposed. It

consists in the fact that the filling of microcracks and surface defects during the modification by ultradispersed particles blocks their development during wear and deformation.

Main results

1. The technology of mineral coatings does not create a coating as such, but creates a modified layer with a granular structure that differs from the bulk structure of the metal. The cumulative use of processes of mineral coating technology creates the effect of bulk compression of the base metal and mineral in the zone of plastic deformation, and, as a consequence, hardening of the surface layer. This "cold" treatment creates a thin layer containing mineral particles that concentrate in the previously created micro cavities. As a result, a modified layer with a high hardness and wear resistance is formed in the surface layer of the sample of steel or titanium alloy.

2. Results of complex studies of the mechanical properties of metal properties of samples modified by minerals, including using the sclerometry method. The wear resistance of the surface of the titanium alloy VT6 (Ti-Al-V), modified by minerals, increased more than 4-fold as compared to the wear resistance of the surface without modification.

3. Results of the investigation of the temperature dependence in the range of 30-140 °C of the coefficients of friction of samples from low-carbon steels 12X13 and 18X2N2M with minerals modified by layers. It was found that under the experimental conditions (contact pressure 550-600 MPa, displacement speed 4-74 mm / s, Mobil SHC 639 oil), the coefficient of friction remains practically constant for samples with mineral coatings (increases by no more than 10% of the coefficient of friction at room temperature), in contrast to the friction coefficient of

unmodified samples, including hardened ones, for which its value increases by more than 50% for the same tests.

List of published articles, where the main scientific results of the dissertation are reflected

The materials of the thesis were published in 16 printed works, 3 of them are included in the Scopus citation system (of which 2 articles are in scientific journals included in the list of the Higher Attestation Commission of the Russian Federation and 1 publication in the collection of reports of the international conference included in the Scopus and Web of citation system Science), 3 articles in scientific journals included in the list of the Higher Attestation Commission of the Russian Federation, 3 articles in scientific journals and 7 publications in collections of reports and conference proceedings.

The main results of the dissertation research were published in 7 papers with a total volume of 7.4 pp, the author's personal contribution is 6.9 pp.

Articles published by the author in peer-reviewed scientific journals, included in the international abstract databases and citations Scopus and Web of Science
(Skazochkin AV - articles in Scopus:
https://www.scopus.com/authid/detail.uri?authorId=6508248800):

1. Skazochkin A.V., Useinov A.S., Kislov S.V. Surface hardening of titanium alloy by minerals / Letters on Materials / 2018, No. 8 (1), pp. 81-87. DOI: 10.22226 / 2410-3535-2018-1-81-87. (Scopus, 1.1 p.p.)
2. Kislov S.V., Kislov V.G., Balasch P.V., Skazochkin A.V., Bondarenko G.G. and Tikhonov A.N. Wear resistance of a metal surface modified with minerals / Materials Science and Engineering / IOP Conf. Series: Materials Science and

Engineering 110 (2016). DOI: 10.1088 / 1757-899X / 110/1/012048. (Scopus, Web of Science, 0.52 pp)

3. Kislov S.V., Kislov V.G., Skazochkin A.V., Bondarenko G.G., Tikhonov A.N. Effective mineral coatings for hardening the surface of metallic materials. Metallurgy (Metally), 2015, No. 7, p. 558-564. DOI: 10.1134 / S0036029515070095. (Scopus, 1.1 p.p.)

Articles published by the author in the leading peer-reviewed scientific journals and publications recommended by the Higher Attestation Commission:

4. Skazochkin A.V., Useynov A.S., Kislov S.V. Surface hardening of titanium alloy by minerals / Letters on materials. 2018. T.8, No. 1 (29). C.81-87, (1.1 p.p.)

5. Kislov S.V., Balash P.V., Kislov V.G., Skazochkin A.V. Research of some tribological parameters of a metal surface modified by minerals / magazine "Pumps. Turbines. Systems », 2016, №4, p.35-45, (1,2 p.p.)

6. Balash PV, Kislov SV, Skazochkin AV Small innovative enterprise: opportunities for technology development and business scaling, "Innovations" magazine, 2015, №12, p.95-105, (1.6 p.p.)

7. Kislov SV, Kislov VG, Balash PV, Skazochkin AV, Bondarenko GG, Tikhonov A.N. Increase of wear resistance of threaded joint of steel tubing during mineral coating / Oil and gas business, 2015, №4, p.216-230, (0.8 p.p.)

8. Kislov SV, Kislov VG, Skazochkin AV, Bondarenko GG, Tikhonov A.N. Effective mineral coatings for hardening the surface of metallic materials / Metals, 2015, №4, p.56-63, (1,1 p.p.)

Articles published by the author in other publications:

9. Kislov S.V., Balash P.V., Kislov V.G., Skazochkin A.V. The use of mineral coatings to improve the wear resistance of chromium-containing corrosion-resistant steels / Chemical Engineering, 2016, No. 8, p.20-30, (0.9 p.p.)

10. Kislov S.V., Balash P.V., Kislov V.G., Skazochkin A.V. Mineral multifunctional coatings - a new type of protective coatings for structural materials / Corrosion of the territory of "Neftegaz", 2016 No. 3, pp. 80-84, (0.8 p.p.)

11. Kislov S.V., Balash P.V., Kislov V.G., Skazochkin A.V. Mineral coatings - a new word in surface engineering / Valve construction, 2016 No. 4 (103), from 58-63, (0.8 p.p.)

Publications of reports in the collections of conference reports:

12. Skazochkin A.V., Bondarenko G.G., Kislov S.V. On the possibilities of a new technology of mineral coatings to improve the wear resistance of the metal surface when creating parts of vacuum technology, "Vacuum Technology, Materials and Technology." Collective monograph. Materials of the XIII International Scientific and Technical Conference. Edited by Doctor of Technical Sciences, Professor S.B. Nesterov. M .: NOVELLA. 2018. p.78-82.

13. Kislov S.V., Kislov V.G,. Skazochkin A.V., Bondarenko G.G., Tikhonov A.N. New technology to increase the wear resistance of metal surfaces and the possibility of its use at aerospace enterprises / In the collection: New materials and technologies for deep processing of raw materials are the basis for innovative development of the Russian economy. Collection of reports of the II International Scientific and Technical Conference (dedicated to the 85th anniversary of the foundation of the "VIAM" - the leading material science center of the country), 2017. p.26-38.

14. Bondarenko G.G., Skazochkin A.V., Kislov S.V., Kislov V.G. On Some Properties and Practice of Using Mineral Coatings / Proceedings of the 10th International Conference "(Zakopane, Poland, June 27-30, 2017). Poland, Lublin University of Technologies, 2017, p.50.

15. Skazochkin A.V., Bondarenko G.G., Tikhonov A.N. On some properties and practice of using mineral coatings / Collection of materials of the All-Russian Scientific Conference "New Materials. Devices. Technology », December 9, 2016,

Moscow, MIEM NIU« Higher School of Economics ».- M.-MIEM NIU HSE, 2017, p.12-15
16. Kislov S.V., Kislov V.G., Balash P.V., Skazochkin A.V. Using the technology of mineral coatings to increase the life of parts at enterprises of the energy sector / Prospects for the development of new technologies in the energy sector of Russia: conference materials // International Scientific and Practical Conference, October 27-28, 2016, Moscow-M .: "VTI", 2016 .-p. 229-234
17. Bondarenko G., Kislov S., Skazochkin A., Kislov V., Balash P., Tikhonov A. New Mineral Coverings: Technology, Opportunities, Commercialization / Proceedings of the 9th International Conference "New Electrical and Electronic Technologies and their Industrial Implementation "(Zakopane, Poland, June 23 - 26, 2015). Poland, Lublin University of Technologies, 2015, p.99.
18. Kislov S.V., Kislov V.G., Balasch P.V., Skazochkin A.V., Bondarenko G.G., Kulagin V.P., Tikhonov A.N. Collection of Proceedings of the XIII Russian-Chinese Symposium "New Materials and Technologies." Under the general editorship of Academician RAS KA Solntsev. In 2 volumes, Moscow: Intercontact Science, 2015, p.296-299.

Personal contribution of the author in the development of the problem

The author plays the main role in carrying out experiments on the complex study of the tribological properties of mineral coatings on various materials and details, studying the change in the microstructure of the modified layer, performing a study of the temperature dependence of the coefficient of friction of samples from low-carbon steels with mineral-modified layers, processing and generalization of the results obtained. Personal participation of the applicant consisted in the formulation of research tasks and their solution, obtaining experimental results on wear resistance and other mechanical properties, interpreting experimental data obtained, writing articles and preparing reports.

Approbation of work

The main results and provisions presented in the paper were reported at the following conferences:

- XIII International Scientific and Technical Conference "Vacuum Technology, Materials and Technology" (Moscow, Sokolniki Culture & Exhibition Center, 2018, April 24-26, 2018). Report "On the possibilities of a new technology for mineral coatings to improve the wear resistance of a metal surface when creating parts of vacuum technology";
- 10th International Conference "New Electrical and Electronic Technologies and their Industrial Implementation" (Zakopane, Poland, June 27-30, 2017). The report "On Some Properties and Practice of Using Mineral Coatings";
- 2nd International Scientific and Technical Conference "New Materials and Technologies for Deep Processing of Raw Materials - the Basis of Innovative Development of the Russian Economy" (Moscow, VIAM, June 27, 2017). The report "New technology of increase of wear resistance of a metal surface and possibility of its use at the enterprises of an aerospace industry";
- International scientific and practical conference "Prospects for the development of new technologies in the energy sector in Russia" (Moscow, JSC "VTI", October 26-27, 2016). Report "The use of technology of mineral coatings to increase the life of parts at enterprises of the energy sector";
- All-Russian Scientific Conference "New Materials. Devices. Technologies » (Moscow, MIEM HSE, December 9, 2016). Report "On some properties and practice of using mineral coatings";
- 9th International Conference "New Electrical and Electronic Technologies and their Industrial Implementation" (Zakopane, Poland, June 23 - 26, 2015). Report "A New Mineral Covering: Technology, Opportunities, Commercialization".
- XIII Russian-Chinese Symposium "New Materials and Technologies" (Kazan, Russia, September 21-25, 2015) Report "Mineral coating: technology features, commercialization opportunities".

Conclusions

As a result of the thesis, new data were obtained on the change in the surface structure, as well as on the mechanical properties of some structural materials (low-carbon steels, titanium and aluminum alloys) modified with ultradispersed mineral particles.

When conducting structural studies it was found that the technology of mineral coatings does not create a coating as such, but creates a modified layer with a granular structure that differs from the bulk structure of the metal. Surface treatment by technology creates a thin layer containing mineral particles, concentrating in pre-created microcavities. As a result, a modified layer with a high hardness and wear resistance is formed in the surface layer of the sample of steel or titanium alloy. Filling in the process of modification by ultradispersed particles of microcracks and surface defects blocks their development during wear and deformation.

The study of the mechanical properties of the surface of a titanium alloy VT6 modified by minerals, using the sclerometry method, showed that the wear resistance of the surface increased by more than 4 times compared with the surface without modification. Experimental data obtained by sclerometry minimizing the effect of the substrate can be used later to calculate and construct models of the metal surface of minerals modified with ultradispersed particles.

Investigation of the temperature dependences of the coefficient of friction of samples from steel modified by minerals in the range 30-140 ^{0}C
showed that the coefficient of friction remains practically constant for samples with mineral coatings (increases by no more than 10% of the coefficient of friction at room temperature), in contrast to the friction coefficient of unmodified samples, including hardened ones, for which its value increases more than by 50% for the same tests. The results of these studies can be used to predict the behavior of

various parts with mineral coatings during operation in various devices and mechanisms.

In carrying out the work it was established that the degree of wear of the toroid from alumina conjugated to disks of steel 12X13 with mineral coating when rotating in water is below the level of registration of the degree of wear and cannot be quantified in the experiment (water temperature T = 23 ° C, linear velocity v = 0.1 m /s, the total displacement length s = 2 km). The value of the coefficient of volumetric wear of the alumina toroid, conjugated with mineral-coated discs when rotating in water, is at least two orders of magnitude smaller than the values of the coefficient of volume wear during rotation with uncoated discs.

In the process of research, several applied problems have been solved that make it possible to use the technology of mineral coatings to increase the life of parts used in the oil and gas industry enterprises, enterprises manufacturing shut-off valves and others. Tribotechnical tests of shut-off valve simulators showed a significant increase in wear resistance of mineral-coated samples (by 4-5 times) as compared to the wear resistance of initial samples from various types of steel (20X13, steel 20, 45X steel). Samples-simulators showed no signs of setting, passed the plasticity test (2-angled bend with a deflection of 0.5 mm), corrosion resistance in a chamber of high humidity (temperature (40 ± 3) 0C, relative humidity of ambient air (97 ± 3) %). The set of pipe samples nipple coupler made of Magnadur 501 steel with a wear-resistant mineral coating successfully withstood the planned number of screwing-unscrewing cycles (400 cycles), which is more than an order of magnitude more than a set of samples from this steel without mineral coating (30 cycles). The test certificates presented in the Appendix to the dissertation, commissioned by industrial enterprises, show that the application of mineral coating technology has an intersectoral coverage (metallurgy, shipbuilding, power engineering, mining, gas and oil production), potentially can be of considerable scale as on the socio-economic effect, and on the export potential. On the basis of the results of the study, it can be concluded that

mineral coatings are a promising technological tool for increasing the wear resistance of various parts, assemblies and mechanisms for use in various industries.