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Solid lubricant ceramic coatings on aluminium and its alloys

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Abstract. Intensive development of space technology, chemical and electronic industries, modern machine-building industries requires creation of antifriction materials with significantly higher tribotechnical properties. Ceramic materials based on aluminium oxide and formed in a microarc discharge plasma on the surfaces of aluminium parts are very promising. However they can not work in friction nodes without lubrication and intensive cooling. Their antifriction properties might be improved by including micro- and nanoscale particles of an antifriction filler in a ceramic matrix to obtain ceramic coatings with solid lubricant properties. The authors consider the basics of the original microarc technology that makes it possible to obtain new composite solid lubricating coatings, which consist of various aluminium oxides, as well as solid lubricant dispersed inclusions, such as graphite, molybdenum disulphide and magnetite. They also analyse the effect of inclusion of highly dispersed filler particles from a colloidal electrolyte on the coating formation process. In order to improve the quality of coatings, it is suggested to use filler particles coated with solvated shells. An electrochemical installation for obtaining a composite coating has been improved to create an increased concentration of dispersed phase particles in the coated sample surface area. The paper investigates tribotechnical properties of the obtained wear-resistant oxide coatings on an aluminium alloy. It is shown that the inclusion of special dispersed particles in its composition can ensure a stable and continuous operation of a friction unit, reduction of a friction coefficient and linear wear under conditions of lubricant deficit. A ceramic coating with a molybdenum disulphide has shown the highest antifriction characteristics.

1. Introduction

Nowadays, the problem of ensuring the effective operation of the bearing units of special equipment without lubricating them both with liquid and a lubricating grease has become important again. Several decades ago, the problem of “dry” friction units was solved by using a polymer composition, for example, based on tetrafluoroethylene or polyamide, to produce one of the friction pair elements. People have achieved significant progress in developing antifriction polymers. These materials have generally satisfied the requirements in terms of a friction coefficient, wear resistance, strength, etc. However, recently, as space and military equipment, chemical and electronic industries, as well as textile and weaving factory has been developing intensively, the need in antifriction materials with significantly higher properties has appeared. For example, the proposed composite coatings are extremely important for “dry” friction units installed in modern and advanced bearings that work with gas lubrication, since they make it possible to increase the reliability and durability of supports by increasing the number of “start-stop” cycles and more long-duration preservation of the permissible sizes of working microgaps. We should note that gas-lubricated spin-axis bearing system contribute to a significant increase in the quality of such technically advanced products as gyroscopes, super precision gyroinstruments, super centrifuges, laser measuring instruments, turbomachines for nuclear industry, precision metal processing equipment, etc.

Perspective constructional materials for technically more perfect dry-friction tribounits are ceramic materials based on aluminium oxide, which were obtained in a microarc plasma discharge (microarc oxidation method) [1]. Coatings can be applied to internal and external surfaces of complex parts and do not require preliminary preparation of the original surface. Such coatings have a thickness of up to 200 μm, a complex of high mechanical properties, good adhesion to a base coat. They are heat-resistant, but they do not work in friction nodes without lubrication and intensive cooling. Now there is a need in expanding the range of physical, mechanical and antifriction properties of coatings by obtaining composite coatings according to the abovementioned technology [2]. For this purpose, it is proposed to include antifriction filler micro- and nanoscale particles in a ceramic matrix to obtain solid-lubricating ceramic coatings. This approach allowed creating unique diamond-containing ceramic coatings for an abrasive tool [3, 4].

2. Purpose of the study

The purpose of this work is to develop the basics of the technology for obtaining solid-lubricating composite ceramic coatings on an aluminium alloy with antifriction fillers based on graphite, molybdenum disulphide and magnetite, by microarc oxidation.

3. Description of the conducted research

3.1. Methodical issues of the experimental research

As the basic research materials, the authors have chosen aluminium-based alloys (D1 GOST 4784-74) that are widely used in technology.

Composite coatings with dispersed powders were formed in electrolytes containing disperse materials as filler. These materials modified the structure of the hardened surface layer during oxidation. A nanodisperse phase of a ceramic coating was a magnetite, which is able to increase mechanical properties of coatings and should help reduce friction as a result of reducing adhesion bonds between contacting surfaces.

High-dispersion magnetite was obtained by chemical condensation proposed by W.S. Elmore in 1938. It is based on the following reaction:

$$2\ FeCl_3 + FeCl_2 + 8\ NH_4OH \rightarrow Fe_3O_4\downarrow + 8NH_4Cl + 4\ H_2O.$$

The method of chemical precipitation of highly dispersed magnetite assumes neutralization of salts of bivalent and ferric iron by an excess of an aqueous ammonia solution while stirring constantly. The reaction leads to formation of an ammonium chloride. It is separated from a precipitate by repeated washing with distilled water, which prevents coagulation of magnetite particles and ensures adsorption of SAS stabilizer molecules with the surface of magnetite particles. The precipitate of the chemical reaction contains magnetite particles of size 2–20 nm, most of them are about 7 nm. The surface of magnetite particles has a good adsorption capacity, which is necessary for their colloidal stabilization. In order to protect highly dispersed magnetite particles from oxidation and prevent their coagulation, a peptization process was carried out in a sodium silicate solution to create an electric charge on the surface of particles. Aggregative stability of the colloid was achieved by ionic mechanism.

To obtain a dispersed phase of antifriction coatings, except for magnetite, we used finely divided graphite powders (particle size 2–10 μm) (GOST 18191-78) and molybdenum disulphide (MVCh TsMTU 06-01-68), which traditionally possess high antifriction properties. Glycerine and triethanolamine were surfactants for modifying the surface of particles.

During oxidation, additional dispersed components in the electrolyte are transported to the surface of the processed alloy by an inhomogeneous electric field. When falling into a spark discharge combustion zone, they are included in the coating composition (in fact, this is an arc electrophoresis).

There is an improved laboratory electrochemical installation for producing a composite coating. It includes an electrolyte active mixing system in order to create an increased concentration of dispersed phase particles in a surface area of a coated sample.

In order to test the obtained antifriction composite coatings, we used countersamples from tool hardened alloy steel KhVG (GOST 5950-73) with a hardness of 45–50 HRC.

Tribotechnical tests of composite coatings with a ceramic matrix and various fillers in the medium pressure range were carried out using a friction machine MTP [5], a disk-finger friction scheme. Table 1 shows operating parameters of the installation.

Table 1. Technical characteristics of the MTP installation.

Friction parameters	Varying range
Sliding speed, m/s	0.15—0.95
Diameter of samples, mm	6
Contact pressure, MPa	0.5—15
Relative error of wear measurement	up to 2%
The relative error in friction moment measurement	up to 0.4%

The method for measuring microhardness of thin ceramic coating was performed according to GOST 15150-80 applying small loads on a pyramidal tip with an angle at the vertex of 136° in order to avoid the influence of mechanical properties of the substrate material half-space on the results.

The microstructure of the obtained coatings was studied on an optical module that included a metallographic microscope of the MIM-8 brand and a digital camera (magnification × 2000) connected to a computer via a video card having a frame capture function. This module makes it possible to quickly and accurately determine the relative proportion of pores and dispersed inclusions on the surface of a ceramic sample.

The developed digital methodology for the quantitative evaluation of foreign inclusions in a ceramic composite coating material is a much more accurate compared with standard metallographic methods due to levelling the human factor influence.

A topographic image of a thin section surface in an intense frictional interaction zone at the micro- and nanoscale was obtained using a scanning probe microscope Solver P47H.

3.2. Technological basis for obtaining coatings

A basis for the technology of composite coatings was the existing technology of microarc synthesis of oxide coating on an aluminium alloy. The application of the coating under consideration does not require thorough preliminary cleaning of the surface and complex laboratory equipment. The coating obtained by the known technology has sufficient thickness, high adhesion to a substrate material (Table 2) and high hardness. The main disadvantage of a base coating is a high dry friction coefficient, which is likely to cause jamming of a friction pair and fast fatigue failure of contacting surfaces. Considering this disadvantage, the coating was modified in the direction of reducing the friction coefficient without using a lubricant.

Table 2. The properties of the anodic coating on the aluminium alloy D1, the formation conditions.

Coating thickness, mm	Dry friction coefficient	Linear wear intensity	Microhardness, GPa	Electrolyte composition
0.1–0.3	0.28–0.35	$\approx 13 \cdot 10^{-9}$	11–12	NaOH alkali, sodium silicate, distilled water

This problem was solved by electrophoretic introduction of solid lubricant particles into a ceramic matrix of a coating. The electric current inclusion leads to the growth of a barrier oxide layer on the surface of the coated aluminium sample, which forms a refractory ceramic matrix. At the same time, fine-dispersed solid lubricant particles are deposited and retained from the electrolyte solution by electromagnetic forces on the surface of the sample. They are gradually incorporated into the matrix. Incorporation of fine-grained magnetite from the colloidal electrolyte into the coating of particles did not cause any significant changes in the formation of the coating.

The inclusion of graphite particles in the coating is complicated by its good electrically conductive properties. When electric current is connected, graphite particles settle on the surface of a part to be

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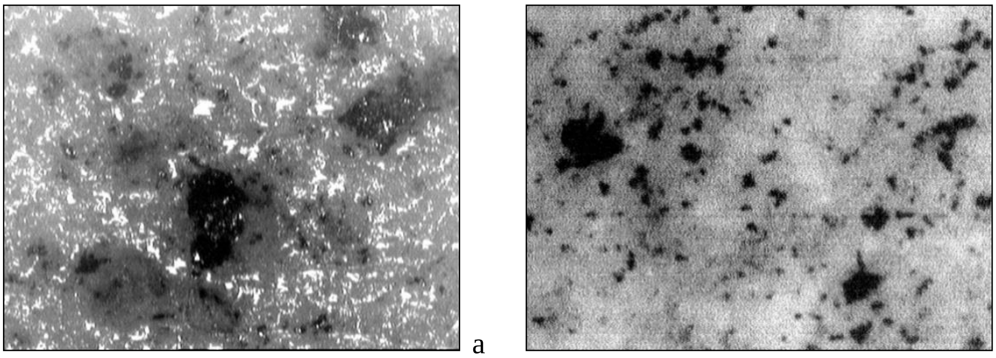
coated and cause corrosion. There is a violation of a surface passive layer and, therefore, nondischarge current flow locations arise.

There are two approaches to coating formation that might solve this problem. According to a first method, the electrochemical coating process is divided into two steps. At the first step, a thin (5–10 μm) technological protective coating is formed on the surface of the sample to be coated in an electrolyte that does not contain graphite particles. At the second step, the ceramic coated sample is placed in an electrolyte containing an elevated concentration of sodium silicate and a finely dispersed (2–10 μm) graphite powder. With the given modes, the process continues until a coating of a given thickness forms. The ceramic coating obtained by this method has a concentration gradient of a dispersed graphite filler. It is completely absent in the layer bordering with aluminium.

The second method for forming the coating uses glycerine as a dielectric film adsorbed on the surface of graphite particles and leading to a decrease in its electrical conductivity. This method gives coatings with a uniform concentration of graphite particles throughout a coating thickness. Non-ionic properties of glycerine determine its choice. Figure 1 shows the microstructure of the coating.



a b

Figure 1. A microstructure of a ceramic composite coating surface with a graphite filler on an aluminium alloy D1: a is in ordinary light; b is in polarized light (×500).

The second material of the dispersed phase is molybdenum disulphide, which has good lubricating properties and is a dielectric, in contrast to graphite. A significant disadvantage of molybdenum disulfide is its relatively high chemical activity. More specifically, during a coating formation it can turn into MoO_2 dioxide and MoO_3 trioxide under the influence of high temperature and an oxidizing environment. They substantially reduce antifriction properties of the resulting coating. To prevent molybdenum disulfide oxidation, glycerine protective properties have also been used.

Table 3 shows the optimal composition of electrolytes worked out as the experimental result. The optimal composition includes dispersed phases of various fillers.

Table 3. The composition of electrolytes for obtaining ceramic coatings with antifriction fillers.

Electrolyte constituent elements	Elements concentration in an electrolyte, wt.%		
	Coating with graphite particles	Coating with molybdenum disulphide particles	Coating with magnetite particles
NaOH alkali	0.1	0.1	0.1
Liquid glass	1.5	1.1	1.5
Dispersed particles	3	4.5	4÷6
Surfactant - glycerine	2	3	-
The rest is distilled water			

3.3. Basic tribotechnical properties of coatings

Tribotechnical studies have confirmed the effectiveness of dispersed solid lubricants in the synthesis of ceramic coatings that are operated in dry friction units. They have also shown the advisability of using surfactants (glycerine) to obtain coatings.

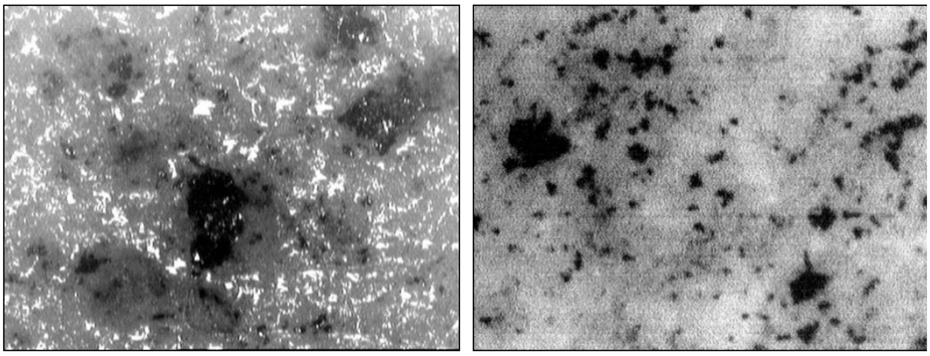
It was shown that the friction coefficient for a ceramic coating with molybdenum disulphide, which was not treated in glycerine, is in the range 0.25–0.5 typical for coatings without filler. This confirms the glycerine protective function and is rationale for using it (or similar in surfactant properties) in obtaining a self-lubricating coating with molybdenum disulphide particles as a dispersed phase.

The test results of the obtained coatings are shown in Table 4. It can be seen from the table that the inclusion of magnetite nanodispersed particles in the coating resulted in an increase in coating microhardness. Apparently, this is due to the fact that the coating became less loose as porosity became half as high. The frictional properties of coatings with magnetite during friction without lubrication have slightly improved, however their overall level is lower than for coatings with solid lubricants.

Figure 2 shows photographs of friction paths on the coating with MoS_2 particles. A countersample is KhVG steel. Dark areas on the friction surface of a specimen with a ceramic antifriction coating and a steel countersample indicate forming of a MoS_2 protective lubricant film on them.

Table 4. The properties of the anodic coating on the aluminium alloy D1, the formation conditions.

Filler material	Coating thickness, mm	Friction coefficient	Linear wear intensity	Microhardness, GPa
MoS_2	0.1 – 0.50	0.07 – 0.11	$5 \cdot 10^{-9}$	10 – 12
Graphite	0.1 – 0.45	0.10 – 0.16	$7 \cdot 10^{-9}$	12 – 14
Fe_3O_4	0.1 – 0.30	0.15 – 0.26	$9 \cdot 10^{-9}$	14 – 17
No filler	0.1 – 0.40	0.11 – 0.25	$15 \cdot 10^{-9}$	12 – 14



a b

Figure 2. Friction surfaces of the composite coating with MoS2 particles: a is a coated sample; b is a counterbody (KhVG steel).

The influence of contact pressure on linear wear intensity of coatings with graphite and MoS2 particles was investigated. In the investigated working pressure range, a ceramic coating with MoS2 filler have shown the highest antifriction characteristics.

A high concentration of molybdenum disulphide particles in the coating material provides friction under conditions of solid lubrication, and therefore a decrease of the friction coefficient and linear wear. As for a composite coating with graphite particles, its linear wear intensity is 1.5–2 higher than the molybdenum disulfide-modified coating has. It is explained by initially lower antifriction properties of graphite and its lower concentration in the coating material.

During the research, the intensity of counterbody linear wear was monitored. There was a slight excess of the counterbody wear rate comparing with this characteristic for a ceramic coating. This is an undoubted advantage of the created composite coatings in comparison with traditional coatings on aluminum, which significantly wear out the counterbody under dry friction conditions.

4. Conclusion

The paper proposes a new approach to the production of self-lubricating composite coatings on aluminium and its alloys in the anode-spark mode. This approach differs from the known one in that a finely dispersed powder of a molybdenum disulphide, magnetite or graphite is added to the electrolyte by a surfactant. The authors have determined tribotechnical properties of self-lubricating composite coatings on aluminium alloys synthesized by the anodic-spark method. Unlike traditional ocidic ceramic materials obtained by microarc oxidation, they have higher antifriction and antiwear properties, which allows them to be used in extreme conditions without additional lubrication with liquid or consistent materials.

Acknowledgments
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