Application features of microarc oxidation technology

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Abstract. The technology of microarc oxidation of valve metals is one of the promising methods for engineering the working surface of friction units of modern technology. As a result of the versatility of the technology, it is possible to obtain composite ceramic coatings and materials of various types. Their properties are set by the electrical modes of material formation, the chemical composition of the electrolyte, and the possible further modification of the ceramic matrix with micro- and nanosized tribofillers. Based on the practical results of their research in the field of creating coatings of various types by microarc oxidation, an analysis is given of the main areas of application of microplasma electrolytic oxidation technology, their advantages over other methods of surface modification, structure and properties of the materials obtained. It is possible to distinguish the modification of the friction surface of a part by the method of microplasma electrolytic oxidation in order to increase its hardness and wear resistance. Good results were obtained in increasing the wear resistance of the hardened working surface of the spinning machine parts, the number of equipment repairs was reduced by more than 20 times. The use of microarc oxidation is promising for the preparation of composite coatings, which are a ceramic matrix in which solid lubricating dispersed particles are embedded. The technology of forming a matrix on aluminum, modified with dispersed magnetite, graphite and molybdenum disulfide, has been developed. According to the results of comparative tribotechnical tests, it was found that the intensity of linear wear of the material filled with MoS_2 is 3 times, and Fe_3O_4 - 1.6 times lower than that of the coatings without filler. Based on the technology of microplasma electrolytic oxidation, an original technology has been developed for obtaining mineral-ceramic material, which is a matrix of aluminum oxide and dispersed diamond inclusions. Abrasive wheels made from this material have a consistently high volumetric cutting ability, 1.5-3.5 times higher than the traditional analogues and are characterized by high diamond retention. The possibilities of microplasma oxidation have not yet been fully explored, the most promising direction being the creation of nanostructured coatings for a specific technological task.

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1 Introduction

One of the promising methods for engineering the working surface of friction units in modern technique is the technology of oxidation in electrolytic plasma or microarc oxidation (MAO) [1, 2]. The oxidation process consists in the formation of a hardened ceramic layer under the action of high stress on the surface of metals with the strongly marked valve properties (Al, Mg, Ti, Zr, Nb, Ta, Be and alloys based on them). The technology of microplasma modification of the surface of parts is in demand for the modification of tribounits in the machine building, oil and gas industry, instrument making, radio electronics, transport, aviation and space, and other industries [1–9].

The characteristics of the materials formed in the electrolyte plasma are determined by the combination of physical and mechanical parameters of the base materials, transitional and working ceramic layer. The properties and structure of the oxide ceramic layer, in turn, are determined by the electrical modes of material formation, the chemical composition of the electrolyte, and the possible further modification of the ceramic matrix with micro- and nanosized tribofillers [3, 4, 10]. As a result of the universality of the technology, it is possible to obtain composite ceramic coatings and materials characterized by high tribomechanical, electrical insulating, and thermophysical properties. At present, technological modes have been developed for obtaining a fairly wide range of MAO materials.

In general, the stages of coating formation during microplasma oxidation are similar to the formation of MAO coatings of various types. But seemingly minor details of the technology that are insignificant at first glance can lead to diametrically opposite results, for example, to obtain not an antifriction, but an abrasive material [11]. The technologies for obtaining promising composite coatings, which are a ceramic matrix in which solid lubricating dispersed particles (polymers, graphite, modibdenum disulfite, nanocorundum, etc.) are embedded, are largely variable [7, 12, 13].

It is rather difficult for the technologists and design engineers of machine-building enterprises to decide on the diversity of possible methods for optimal modification of the surface of parts. Many promising technologies of microplasma electrolytic oxidation are known in scientific circles and have not yet been widely used in real mechanisms. The nomenclature of equipment, required to obtain a composite ceramic coating with desired physical and mechanical properties, is not always clear.

The objective of the paper is to analyze the main directions of application of the microplasma electrolytic oxidation technology, their advantages over other methods of surface modification, the structure and properties of the materials obtained, for a wide range of technologists and design engineers of modern equipment.

2 Main applications of microplasma electrolytic oxidation technology

1. Modification of the friction surface of a part by microplasma electrolytic oxidation in order to increase its hardness and wear resistance. This direction is the most traditional [1, 2]. In the process of oxidation, a three-layer coating is formed on the surface of the part from the transition, working and outer technological layers. A thin transition layer (thickness 0.01 - 0.1 μm) ensures high adhesion of the ceramic coating to the base metal. The working oxide layer, up to 100 μm thick, is the most functional, it is a complex structure of α -, β - and γ - modifications of aluminum oxides. Modification α-Al_2O_3, or corundum, prevails, as it is the most stable. This coating layer has low porosity and, thanks to corundum, it combines high microhardness, contact rigidity and wear resistance with resistance to corrosion. The outer technological layer has a thickness of up to 200 μm, it has

a significantly lower hardness compared to the working layer, but greater porosity, in fact, it has a loose structure. In the case of oxidation in an alkaline electrolyte with the addition of liquid glass, the technological layer consists of $3Al_2O_3 \cdot 2SiO_2$ mullite. At the end of the formation of the coating, it is advisable to remove the loose technological layer by grinding or sandblasting. The working oxide layer directly involved in the frictional contact has a microhardness of up to 20 HV and in terms of wear resistance this coating is comparable to tungsten carbide.

Compared to known oxidation techniques for aluminium and its alloys, e.g. electroplating, MAO is the most expensive, complex, and energy-intensive. However, the advantages of microplasma electrolytic oxidation of coatings due to unique tribotechnical properties and their significant thickness compared to coatings obtained, for example, by anodizing (layer thickness up to 20 μm) make this technology the most competitive and efficient in the long term.

The most cost-effective is hardening by microplasma electrolytic oxidation of friction surfaces of friction pairs: plain bearings, gears, pulleys, sliding guides, mechanical seals for internal combustion engines, etc. [1, 3, 5-8]. It has been found that the modification of the units of the cylinder-piston group results in an increase in wear resistance by a factor of 10-15 [5].

This type of coating is normally applied in the presence of a lubricant. However, we have obtained good results for increasing the wear resistance of the working surface of spinning machine components operated under dry friction conditions. The durability of the spinning rotors has increased, their service life has increased, production wastes have decreased, and the number of equipment repairs has decreased by more than 20 times (Fig. 1).

Fig. 1. Friction unit of a spinning machine modified by microplasma oxidation.

2. Modification of the friction surface of parts made of light metals (Al, Ti, Mg and their alloys) by microplasma electrolytic oxidation in order to replace heavy metal alloys or expensive composite materials. Surface modification of friction surfaces of light metal parts (Al, Ti, Mg and their alloys) by microplasma electrolytic oxidation, in order to replace heavy metal alloys or expensive composite materials. In mechanical engineering, tribounits hardened by the MAO method are used to replace alloyed steel, while achieving a multiple increase in wear resistance, material consumption and heat load, a reduction in mechanical costs by 40–50%, and an increase in efficiency by 2–15% [1, 5]. It is also necessary to note a significant increase in the dynamic characteristics of moving tribounits, since the density of aluminum is almost 3 times lower than the density of steel.

Reducing the material consumption combined with maintaining and increasing the hardness and wear resistance of the traditional friction units is especially important in the aviation, space and shipbuilding industries. In the aerospace industry, the maximum reduction in the mass of the structure being developed is important, so even the replacement of individual elements is of great importance. In particular, it has been shown that replacement of steel or titanium in the spacecraft opening jaws by micro-arc oxidation-modified aluminium alloy AMg6M is justified [9]. Hardened parts made of lightweight structural material provide high reliability of the unit operation under conditions of vibration loads, increased wear, low temperatures and vacuum. Hardened parts made of lightweight structural material provide high reliability of the unit operation under conditions of vibration loads, increased wear, low temperatures and vacuum.

3. Application of microplasma electrolytic oxidation technology in order to restore the original dimensions of worn parts, while increasing their wear resistance and durability. This direction is most relevant for parts of agricultural, mining equipment, in modern conditions of machine-building and car repair industries. A characteristic feature of the MAO technology is an increase in the overall dimensions of the part during the oxidation process. The formed working layer grows inward and outward from the original surface of the part. The technological layer significantly exceeds the original dimensions of the surface. This feature can be used in repair production. Without additional ways to compensate for worn material, it is possible to increase to 0.1 мм of a wear-resistant ceramic layer [10, 13, 14]. Technologies are known that allow the use of microplasma electrolytic oxidation not only for parts made of valve metals. It is possible to circumvent this limitation by preliminary application, for example, to a steel surface of aluminum-containing compositions and subsequent modification [15].

4. The use of microarc oxidation to obtain a ceramic matrix, into the pores of which solid lubricants can be introduced. This method is used in the case of the functioning of tribocouples in conditions of dry friction and limited supply of lubricant, especially in heavily loaded friction units [4, 8]. The method is possible due to the porosity of the resulting ceramic coating, and the pore sizes (0.01–10 μm) and their concentration (5–50%) can be controlled by the electrotechnical mode of microplasma electrolytic oxidation and the composition of the electrolyte. The range of the fillers used is quite wide: polymeric materials (fluoroplastics, polyamides), micro- and nanostructured graphite, molybdenum disulfite, copper oxide, magnetite, etc.

The technologies for introducing various fillers into the ceramic matrix also differ significantly, which is due to the electrical properties of solid lubricants and, accordingly, their effect on the oxidation process. For example, when modifying the MAO coating with carbon nanosized materials, they are introduced directly into the base electrolyte [4, 16], while the rate of formation of the ceramic layer increases, its thickness increases, the structure becomes more uniform, and the porosity decreases. When modifying an MAO coating with particles of CuO nanopowder, the technology involves two stages: the formation of a ceramic matrix and the direct introduction of copper oxide by arc electrophoresis, directly into a thin surface layer of the coating [8].

We have obtained good results in the modification by microplasma electrolytic oxidation of a matrix formed on D1 aluminum with dispersed magnetite, graphite, and molybdenum disulfide [4]. The introduction of finely dispersed magnetite particles into the colloidal electrolyte did not significantly affect the oxidation process. Molybdenum and graphite disulfide particles required modification with a surfactant when introduced into the electrolyte. Comparative tribological tests of the obtained solid-lubricating composite materials confirmed their advantage over the traditional MAO coating, as well as stable performance under extreme conditions without additional lubrication with liquid or consistent materials (Table 1).

5. Application of microplasma electrolytic oxidation technology to obtain innovative materials. The synergy of the properties of the matrix materials, electrolyte, and dispersed fillers transformed in the process of microplasma synthesis makes it possible to obtain new unique materials with a wide range of applications.

We have developed an original technology for obtaining mineral-ceramic material, which is a matrix of aluminum oxide and dispersed diamond inclusions [11]. The workpiece for the product is formed from a diamond-aluminum mixture by powder metallurgy method. Dispersed diamond grains are pre-coated with copper to protect against excessive oxidation and as an additional antifriction factor [17]. The mineral-ceramic layer is formed on the surface of the part in the process of microplasma synthesis. When analyzing the technology, the optimal ranges for varying the relative density of workpieces, the degree of metallization of diamonds with copper, and the composition of the electrolyte were determined.

Table 1. Formatting sections, subsections and subsubsections.

Filler material	Coating thickness, μm	Friction coefficient	Linear wear intensity	Microhardness, HV
MoS_2	0.1-0.50	0.07-0.11	$5\ 10^{-9}$	10-12
Graphite	0.1-0.45	0.10-0.16	$7\ 10^{-9}$	12-14
Fe_3O_4	0.1-0.30	0.15-0.26	$9\ 10^{-9}$	14-17
Without filler	0.1-0.40	0.11-0.25	$15\ 10^{-9}$	12-14

Evaluation of the frictional properties of the obtained material showed that the grain size of diamonds has a decisive influence on the tribotechnical characteristics and the area of its practical application. When using diamonds with a high grain size (>28/20), a mineral-ceramic material with high cutting characteristics is obtained (Fig. 2). Abrasive wheels made from this material have a consistently high volumetric cutting ability, 1.5-3.5 times higher than traditional analogues and they are characterized by high diamond retention (Fig. 3).

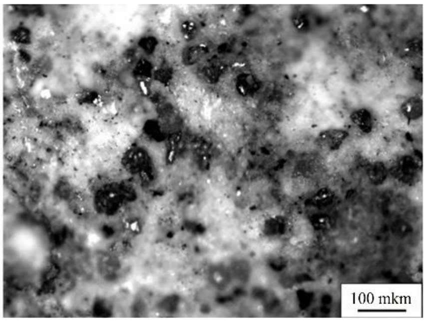

Fig. 2. Structure of the surface of the mineral-ceramic material. Diamond grain 80/63.

Fig. 3. Abrasive wheels with a cutting layer of mineral-ceramic material.

Mineral-ceramic materials with a fine diamond grain (< 20/14) are characterized by high anti-friction properties in conditions of deficiency and absence of lubricant (Fig. 4). This characteristic is explained by the formation of inclusions of free solid-lubricant graphite in the ceramic matrix, which was formed during the partial phase oxidation of diamond.

6. Modification by microplasma electrolytic oxidation of aluminum parts to protect them from aggressive environments: chemically active solutions, seawater, extreme weather conditions, etc. [3, 9, 10, 18]. It was found in [19] that, at temperatures up to 870°C, MAO coatings on titanium alloy Ti-6Al–4V 45–50 µm thick, retained high adhesion to the substrate and surface density without signs of pitting. The corrosion resistance of the formed ceramic coatings is significantly higher than that of traditionally used galvanic coatings. The high environmental friendliness of microarc oxidation, as opposed to the galvanic method, which is carried out in aggressive electrolytes and requires washing, degreasing, and etching. The use of polymer-based varnishes as a filler MAO matrix can be used as an undercoat for painting in critical tribo-products used in aggressive environments. To apply a sublayer for painting, it is enough to form a coating with a thickness of 5-10 µm, which reduces the cost of obtaining the product.

It is promising to strengthen tribosurfaces of friction units lubricated with modern magnetic lubricants by microplasma electrolytic oxidation [20]. In addition to very good anti-friction and anti-wear properties, magnetic lubricating media have a corrosive effect on the contact surfaces. Agglomerates of magnetic particles formed in magnetic oils or liquids also wear abrasive surfaces. Microplasma modification of the surface layer of a part into a ceramic material makes it possible to neutralize the negative effect of the aggressive action of such lubricating media.

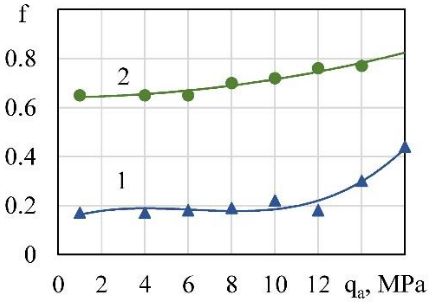

Fig. 4. Friction coefficient for MAO coatings: 1 – diamond-containing material, 2 – D16.

We have developed a technology for obtaining a corrosion-resistant decorative coating by microarc oxidation method. In order to reduce energy consumption, the process occurs in two stages in different electrolytes [21]. A technological layer is formed in the standard electrolyte, and then the components that determine the color of the protective and decorative layer are added to the second electrolyte (Fig. 5). The microhardness of the formed coating is ≈ 5 – 10 HV, the thickness is sufficient to ensure operational characteristics ≈ 20–30 µm.

Fig. 5. Protective and decorative coating obtained by microplasma electrolytic oxidation.

3 The conclusion

The technology of microplasma electrolytic oxidation makes it possible to modify the surface of valve metals by forming a wear-resistant and high hardness ceramic layer on them, which can be supplemented with various types of fillers, both solid lubricants and abrasives. The main applications for such coatings and materials are in friction units, with the surfaces formed to provide stable performance and wear resistance under high loads, temperatures and aggressive environments.

The areas of application of microplasma electrolytic oxidation technology are not limited to the examples given. Technologies have been developed for producing bioactive, electrical insulating, light engineering, and catalytically active ceramic composite materials. The possibilities of microplasma oxidation have not yet been fully explored, and the functional purpose of MAO coatings will be expanded. The most promising direction seems to be the creation of nanostructured coatings for a specific technological task. The use of nanosized additives (metals, oxides, borides, carbon nanotubes, fullerenes, ultrafine particles of detonation synthesis) opens up the possibility of transition of materials to the nanocrystalline state, which opens up fundamentally new properties of a substance.

References

1. N. Y. Dudareva, P. V. Ivashin, R. F. Gallyamova, A. Y. Tverdokhlebov, M. M. Krishtal, Metal Science and Heat Treatment, **62** (2021)
2. P. I. Butyagin, Perspektivnye Materialy, **5** (2021)
3. A. V. Chavdarov, V. A. Denisov, Nexo Revista Científica, **34** (2021)
4. A.N. Bolotov, V.V. Novikov, O. O. Novikova, Physical and Chemical Aspects of the Study of Clusters, Nanostructures and Nanomaterials, **10** (2018)
5. M. B. Sedelnikova et al., Russian Physics Journal, **64** (2021)
6. S. S. Arbuzova, P. I. Butyagin, A. V. Bol’shanin, A. I. Kondratenko, A. V. Vorob’ev, Russian Physics Journal, **62** (2020)
7. P. Wang et al., International Journal of Electrochemical Science, **14** (2019)
8. X. Yang, L. Chen, X. Jin, J. Du, W. Xue, Ceramics International, **45** (2019)
9. A. V. Chavdarov, V. A. Denisov, Agricultural engineering, **4** (2021)
10. Y. A. Kuznetsov et al., Russian Journal of Applied Chemistry, **92** (2019)
11. A. N. Bolotov, V. V. Novikov, O. O. Novikova, Obrabotka Metallov, **22** (2020)

12. Y. Xie et al., Jinshu Rechuli/Heat Treatment of Metals, **44** (2019)
13. O. Tchufistov, E. A. Tchufistov, A. N. Zolkin, in Materials Science Forum, **1037** (2021)
14. Y. Kuznetsov et al., Energies, **15** (2022)
15. Y. Kuznetsov et al., Russian Journal of Applied Chemistry, **92** (2019)
16. A. M. Borisov et al., Surface Engineering and Applied Electrochemistry, **52** (2016)
17. A.N. Bolotov, O. O. Novikova, V.V. Novikov, Bulletin of the Tver State Technical University Series «Engineering», **3** (2020)
18. N. S. Chernyshov et al., Novye ogneupory (New refractories), **4** (2020)
19. S. Song et al., Materials and Design, **215** (2022)
20. A. N. Bolotov et al., Bulletin of the Tver State Technical University Series «Engineering», **1** (2019)
21. A.N. Bolotov, O. O. Novikova, V.V. Novikov, Bulletin of the Tver State Technical University, **1** (2013)