Tribological properties of anode-spark coatings on aluminum alloys

O. Dykha*, O. Babak, O. Makovkin, S. Posonskiy

Khmelnitskyi National University, Ukraine
*E-mail: tribosenator@gmail.com

Abstract

It is established that at present the technology of anode-spark coatings in general is well studied. However, the lack of recommendations for the choice of modes of technological processes and tribological characteristics in different operating conditions limit the widespread introduction of this technology. The task of this work was to analyze the processes of anode-spark coatings, improve technology and study the wear resistance of samples processed by this and traditional anode technology. The development of technology for the application of protective coatings on valve metals in the conditions of spark discharge included the choice of electrolyte and mode of operation of the bath: voltage, current density, hydrodynamic conditions and other parameters. Wear resistance tests were performed on a special installation. Structurally, the installation is made in two positions, which allows you to test two samples with different load conditions at a constant sliding speed. The design of the installation implements the friction scheme of the liner shaft. The study of anode-spark coatings in the mode of limiting lubrication was studied in the environment of industrial oil. The wear criterion was the weight wear of the samples according to the results of weight measurements before and after wear. It is established that prolonged electrolysis in the conditions of sparking leads to the formation of anode coatings that exceed in their properties the films obtained by non-sparking oxidation. Comparative studies of the wear resistance of anode-spark coatings and galvanic anode coatings under the same test conditions showed that the wear of anode-spark coatings is almost twice lower for the entire load range. The considered technology is recommended for increase of wear resistance of elements of devices from the aluminum alloys working in the conditions of corrosion and mechanical wear.

Keywords: anode-spark coatings, aluminum alloys, tribological tests, wear, friction coefficient.

Introduction

For a long time, it was believed that the coating formed in the spark mode has lower protective properties than the traditional anode coating. Because of this, the anodizing was usually stopped at a voltage lower than the breakdown voltage. More recently, it has been established that prolonged electrolysis under sparking conditions leads to the formation of fairly thick anode coatings that exceed in their properties the films obtained by sparkless oxidation. Analysis of anode-spark coatings shows that in them, along with the metal oxides of the substrate in large quantities are atoms and groups of atoms that are part of the electrolyte. In the thickness of the amorphous oxide there are areas of the solidified melt. The latter indicates a strong thermal effect of electrical breakdown on the material of the formed oxide. There is every reason to believe that effective anode-spark molding occurs only if the breakdown is thermal.

Analysis of research and publications

As a result of many studies, at present, it is established that the anode-oxide films consist of two layers: a barrier layer, which has a dense structure and is directly adjacent to the oxidized metal, and a porous layer.

The use of electron microscopy has made the most significant contribution to the studied structures of anode-oxide coatings. The results of these tests performed by Keller, Kanter, Robinson and other researchers allowed us to propose a so-called model of a porous anode oxide film based on physical and geometric images.
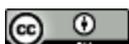
According to this model, in the first seconds of anodizing on aluminum, a non-porous barrier layer is formed, the beginning of the formation of which is associated with the corresponding active oxidation centers on the metal surface. Hemispherical lenticular microelements grow from these embryos. First isolated, then grow and fill the metal surface with the formation of a solid barrier layer. Under the action of local influence of electrolyte ions in the barrier layer, pores begin to emerge, the number of which is associated with the magnitude of the stress of the forming oxide. As a result, an oxidizing element is formed, similar in shape to a spherical segment, the center of which lies in the area of the porous layer. The growth of the anode-spark coating occurs in two ways that run in parallel. The first of them is the formation of the anode coating by the mechanism of growth of oxide films in the metal-oxide-electrolyte (MOE) system, and the second is the formation of chemical compounds on the electrode surface with the participation of electrolyte components. In the process of forming anode-spark coatings. Along with the formation of the film may occur side chemical and electrochemical reactions that lead to unproductive energy consumption and accumulation of substances in the bath, affecting the quality of sludge. The main side processes are the formation of oxygen and hydrogen due to electrolysis in the area of spark discharges. which lead to unproductive energy costs and the accumulation of substances in the bath, affecting the quality of sludge. The main side processes are the formation of oxygen and hydrogen due to electrolysis in the area of spark discharges. which lead to unproductive energy costs and the accumulation of substances in the bath, affecting the quality of sludge. The main side processes are the formation of oxygen and hydrogen due to electrolysis in the area of spark discharges.

Let us pay attention to the most urgent problems in the field of anodic oxidation that are currently being considered.

In work [1], it was noted that tlectrochemical oxidation is an effective wastewater treatment method. Metal oxide-coated substrates are commonly used as anodes in this process. This article compiles the developments in the fabrication, application, and performance of metal oxide anodes in wastewater treatment. It summarizes the preparative methods and mechanism of oxidation of organics on the metal oxide anodes. The discussion is focused on the application of SnO_2, PbO_2, IrO_2, and RuO_2 metal oxide anodes and their effectiveness in wastewater treatment process.

In work [2] it is said that during plasma electrolytic oxidation (PEO) processes, the factors, such as the shape of the specimen, the location of the cathode electrode, and others have a critical influence on the anode (specimen to be treated) current. This may lead to different oxidation dynamics at different locations on the samples resulting in the non-uniform coating thickness and surface properties. In this work, the current through samples made of 2024 aluminum alloy was monitored in a sodium silicate solution during plasma electrolytic oxidation. The experimental results demonstrate that the distance between the cathode and anode affects the anode current and the oxidation efficiency. The current flowing through the front surface of the specimen is larger than that flowing through the back surface of the same specimen. The measured tribological properties and corrosion-resistance agree well with the effects of the current. The front surface exhibits more superior wear and corrosion resistance than the back surface.

In aqueous zinc-ion batteries, metallic zinc is widely used as an anode because of its non-toxicity, environmental benignity, low cost, high abundance and theoretical capacity. However, growth of zinc dendrites, corrosion of zinc anode, passivation, and occurrence of side reactions during continuous charge-discharge cycling hinder development of zinc-ion batteries. In study [3], a simple strategy involving application of a HfO_2 coating was used to guide uniform deposition of Zn^{2+} to suppress formation of zinc dendrites. The HfO_2-coated zinc anode improves electrochemical performance compared with bare Zn anode.

In [4] the deactivation of an IrO_2–Ta_2O_5 coated titanium anode was studied during an accelerated life test at 2 A cm^{-2} in 1 mol dm^{-3} H_2SO_4 solution using CV, EIS, SEM and EDX. The changes of voltammetric charge, double layer capacitance, oxide film resistance and charge transfer resistance of oxygen evolution with time during the electrolysis were monitored. The morphology and surface composition of the oxide anode before and after electrolysis test were analysed. A comprehensive process of deactivation of the oxide anode was proposed based on the test results and analysis.

The wettability of coatings, including ceramic ones, which show considerable promise for the use on bioengineering products, with physical solution (0.9% NaCl) have been studied in [5]. It has been found that the use of coatings of all types under study increases the wetting angles on the surface as compared with the initial metal materials (stainless steel of the 12X18H10T grade, titanium alloy of the BT6-grade, Co-Cr-Mo alloy), which serves as a prerequisite for an improvement in the biocompatibility of implants.

Protective α-Al_2O_3 coatings on the surface of a graphite article have been obtained in [6] by method of electric-arc metallization with aluminum and microarc oxidation (anodic spark process). Investigation of the obtained coating by scanning electron microscopy (SEM), X-ray diffraction (XRD), and proton elastic recoil detection analysis (ERDA) showed good quality of the Al and α-Al_2O_3 coatings on graphite. The proposed technology can be used for obtaining protective coatings in low-accessible sites of graphite articles.

The effect of TiB_2 and CrB_2 additions to the commercial self-fluxing FeNiCrBSiC eutectic alloy on the structurization of electrospark coatings was examined in [7]. The mass transfer kinetics in the electrospark deposition of FTB20 (FeNiCrBSiC + 20% TiB_2) and FCB20 (FeNiCrBSiC + 20% CrB_2) composite materials and commercial self-fluxing FeNiCrBSiC alloy coatings onto steel 45 using an Alier-52 unit was studied. When the energy parameters of electrospark deposition increased, the mass transfer coefficient became higher and the

electrospark coatings thicker and rougher.

The dielectric properties of coatings on AK6 alloy formed with a microarc oxidation method in two electric modes in alkaline-silicate electrolytes are estimated in [8-9]. It is shown that both modes, a galvanostatic mode and an arbitrarily falling power mode in alternating current circuits, make it possible to obtain coatings with a thickness of 30–60 μm, with sufficiently high electrophysical parameters: bulk specific resistance $\rho_v = 3–9 \times 10^9$ Ω m and dielectric strength E = 9–14 V/μm. It is established that higher values of ρ_v and E in the both modes can be achieved in the solutions of 1 g/L KOH + 6 g/L of liquid glass (LG) and 12 g/L of LG. In terms of absolute value, the parameters of the coatings formed in the mode of arbitrarily falling power exceed the same characteristics of the oxide layers formed under conditions of galvanostatic mode by a factor of 1.5–2.5.

Based on the analysis of literature sources, it is established that at present the technology of anode-spark coatings in general is quite well developed. However, the lack of scientifically sound recommendations for the choice of modes of technological processes and characteristics of properties in different operating conditions do not allow the widespread introduction of this technology.

The task of this work was to analyze the processes of anode-spark coatings, improve technology and study the wear resistance of samples processed by this and traditional anode technology.

Selection of technological modes of formation of anode-spark coatings

The development of technology for the application of protective coatings on valve metals in the conditions of spark discharge includes the choice of electrolyte and mode of operation of the bath: voltage, current density, hydrodynamic conditions, etc.

Currently known different types of programmable voltage changes in the bath, pulse and alternating current voltages are selected experimentally, without the necessary theoretical justification. Meanwhile, the electrical regime determines the nature and intensity of discharges and, of course, the temperature conditions on the surface of the anode. With the appropriate choice of electrolyte and electrochemical parameters of the anode-spark sludge, you can get a coating that has high hardness, wear resistance and strong adhesion to the substrate. Appropriate selection of the electrolyte and electrolysis conditions can form a coating that is equal in hardness and wear resistance of corundum and tungsten carbide. The wear of the upper layers is not due to abrasion, but due to chipping of the unevenness of the coating.

To form a coating on aluminum alloys AD31 and B95, we take the current strength range from 1800 A / m² to 2500 A/m² and the ratio of cathode current to anode 1.15. Molding is carried out at voltages from 120 V to 600 V depending on the state and concentration of the electrolyte.

The practical implementation of the anode-spark process always requires careful coordination of metal-electrolyte pairs. One of the simplest and best-known electrolytes was a dilute (2 ... 8 g/l) KOH solution, which makes it possible to obtain a high-quality anode coating on aluminum. Solutions of some acids can be used for this purpose. The first systematic study of the influence of the electrolyte on the possibility of realization of the anode-spark discharge on aluminum was carried out in [7], where the authors studied the properties of solutions of 33 different substances. The investigated electrolytes were divided into 6 groups. The first includes solutions of salts in which there is a fairly rapid dissolution of aluminum ($NaCl$, $NaClO_3$, NaOH, HCl, $NaNO_3$ and Na). The second group combines electrolytes that correspond to the achievement without much effort of the passive state of the metal. It includes H_3BO_3, citric and carbonic acids, as well as their salts. Lactic, adipic and oxalic acids (third group) correspond to less effective passive properties. Weak solution of metal at stationary potential is characterized by substances of the fourth group: H_2SO_4, $(NH_4)2SO_8$, Na_2SO_4. In oxalic acid and its sodium salt, sodium acetate, phosphoric acid (fifth group), the range of voltages at which the spark discharge occurs is narrow. The sixth group includes solutions of KF, NaF, disubstituted phosphate and sodium sulfite. in which the spark discharge is narrow. The sixth group includes solutions of KF, NaF, disubstituted phosphate and sodium sulfite. in which the spark discharge is narrow. The sixth group includes solutions of KF, NaF, disubstituted phosphate and sodium sulfite.

The formation of oxide films from aqueous electrolytes in the sparking mode allows to obtain a coating with much better properties than in the formation in the normal anodizing mode. Analysis of the chemical composition shows that in the composition of the anode-spark coatings, rocks with oxides of the base metal of the strip, in large quantities contain atoms that are part of the electrolyte. Other particles of oxides (iron, chromium) present in the electrolyte are also included in the structure of the coating, forming a composite structure.

Investigation of wear resistance of coatings on aluminum alloys

Samples measuring 5×5×20 mm from materials B 95 and AD 31 were used for the research. The samples must have a quality surface. Overflowing of edges on samples is not allowed.

After machining, the samples are ground on grinders with a grain size of: 400 μm, 200 μm, 80 μm. Then the anode-spark coatings were applied on the experimental setup. After coating according to the developed technological process, the samples were washed and dried with filtered paper. Samples with factory coating were additionally ground on the work surfaces with AP-3 diamond paste. The contact area is 0.25 cm².

Wear resistance tests were performed on a special installation. Structurally, the installation is made in two

positions, which allows you to test two samples with different load conditions at a constant sliding speed. The design of the installation implements the friction scheme of the liner shaft.

The scheme of the test setup is presented in Fig. 1. Rotation counter body 7 receives from the DC motor with adjustable speed. The speed of rotation is controlled by an electronic speed meter PIT-1 (3). The test sample 8 is fixed in the handle 9, which before starting work is balanced in relation to the strain beam 10. The handle of the sample 9 is hinged to the beam. The specified load P is created by a set of loads 12.

Before conducting experiments, the installation system is calibrated. The strain gauges are powered by the UT-4 strain amplifier. Recording of friction forces is performed by a potentiometer type KSP-4.

The body is made of hardened steel 45 (HRC 55) and has the shape of a disk with a diameter of 95 mm and a thickness of 10 mm. Surface roughness Ra = 0, 32 microns
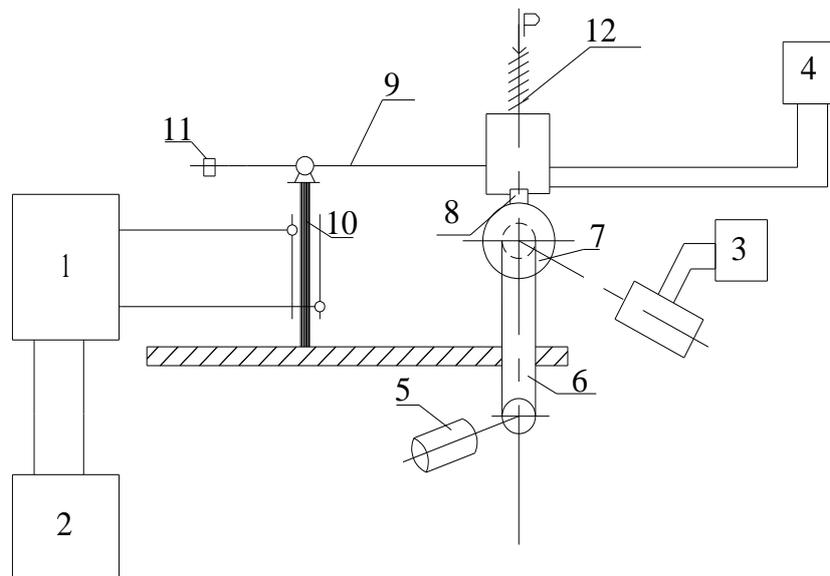
Fig. 1. Scheme of the test installation: 1 - strain amplifier UTCH-1; 2 - potentiometer PCB 4; 3 - sensor-meter of sliding speed; 4 - thermocouple temperature sensor potentiometer EPD-12; 5 - electric motor; 6 - V-belt transmission; 7 - working disk (counter body); 8 - experimental sample; 9 - sample holder; 10 - strain beam; 11 - load - balancer; 12 - loads to create the desired pressure R.

In the study of coatings under dry friction, the efficiency of the anode-spark coatings paired with hardened steel 45 is low with a predominantly abrasive type of wear. Reduced resistance of the coating is caused by brittle fracture (splitting of individual microvolumes). The coefficient of friction during operation is unstable and is measured in a wide range f = 0.3… 0.8.

The study of anode-spark coatings in the mode of ultimate lubrication was studied in the medium of oil I-20, which were saturated samples. The research was carried out before complete wear of the coating formed at different durations of molding. Data on the effect of molding duration on the wear resistance of coatings are given in table 1. The wear intensity is calculated by the formula:

$$U_w = \frac{\Delta G}{S} \, ,$$

where ΔG is the weight wear, g; S is the path of friction, mm.

Table 1

The results of studies of anode-spark coatings

Processing time, τ_{pr}, min	The weight of the sample after processing, G_1, g	Sample weight after the study, G_2, g	Weight wear, $\Delta G \cdot 10^{-4}$, g	The path of friction, $S \cdot 10^3$ m	Wear intensity, $I_W \cdot 10^{-9}$, g/m	Coefficient of friction, f
45	1.05795	1.057890	0.60	16.4	3.658	0.13
60	1.07660	1.076408	1.92	65.6	2.927	0.12
90	1.17212	1.172018	1.025	24.6	4.170	0.14

Figure 2 shows the dependence of wear intensity I_W from the duration of processing (molding) tobr. As can be seen, the optimal duration of molding should be considered up to 60 minutes The coefficient of friction is practically independent of the duration of processing and is measured in the range of 0.12…0.14.
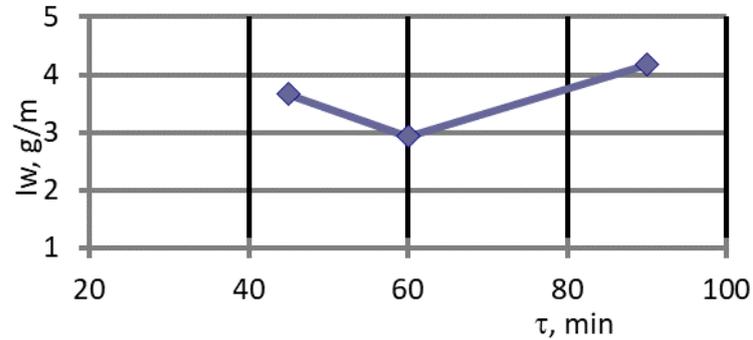

Fig. 2. Dependence of wear intensity of B-95 alloy on molding time

The results of comparative studies of wear resistance of anode-spark coatings and coatings formed by traditional oxidative anodizing technology are shown in table 2 and graphically in Fig. 3. The wear criterion was the weight wear of the samples according to the results of weight measurements before and after wear.

Table 2

Wear test results

Parameters	Meter readings, N	Friction path, $S \cdot 10^3$, m	Weight wear, $\Delta G \cdot 10^{-4}$, g	Friction force, $F_{тp} \cdot 10^{-2}$, N	Coefficient of friction, f
AC P = 0.4 MPa					
1	50	16.4	0.90	40	0.12
2	100	32.8	1.52	44	0.13
3	150	49.2	1.75	43	0.14
ASC P = 0.4 MPa					
1	50	16.4	0.5	7	0.07
2	100	32.8	0.8	9	0.09
3	150	49.2	1.0	8	0.08
ASC P = 0.8 MPa					
1	50	16.4	0.75	20	0.1
2	100	32.8	1.35	24	0.12
3	150	49.2	1.50	26	0.13

With increasing friction path, the coefficient of friction increases slightly to the appropriate value, and then stabilizes. As the load increases, the friction force and the coefficient of friction increase.
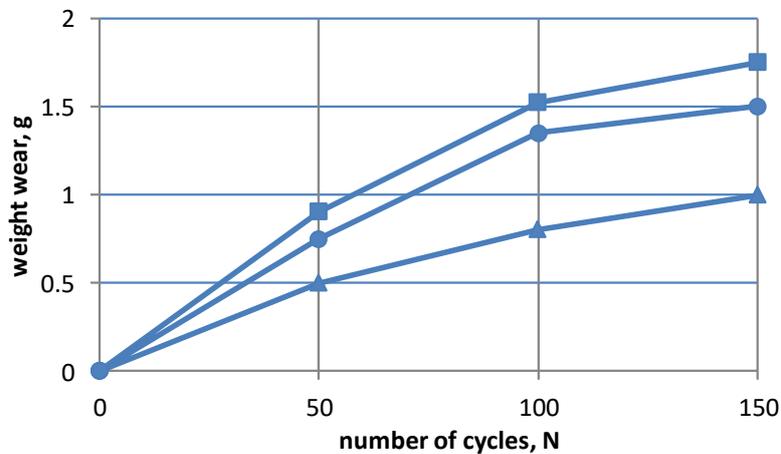

Fig. 3. Dependence of wear of coverings on duration of tests: ▲ - ASC P = 0.4 MPa; ● - ASC P = 0.8 MPa; ■ - AC = 0.4 MPa.

The analysis of the obtained results shows that the anode-spark coating is superior in its properties to the coatings obtained under oxidative anodizing conditions formed in optimal modes, but in the same electrolyte with the same concentration.

The wear resistance of anode-spark coatings in comparison with galvanic anode coatings at the same load was almost 2 times higher. The coefficient of friction of the coatings varied in the range of 0.1 ... 0.14. The optimal duration of coating formation is 60 minutes. It is also established that the wear resistance of anode-spark coatings depends not only on the duration of treatment, but also on other process parameters.

Conclusions

It is established that prolonged electrolysis in the conditions of sparking leads to the formation of anode coatings that exceed in their properties the films obtained by non-sparking oxidation.

Comparative studies of the wear resistance of anode-spark coatings and galvanic anode coatings under the same test conditions showed that the wear of anode-spark coatings is almost twice lower for the entire load range.

References

1. Subba Rao, A.N., Venkatarangaiah, V.T. Metal oxide-coated anodes in wastewater treatment. Environ Sci Pollut Res **21,** 3197–3217 (2014). https://doi.org/10.1007/s11356-013-2313-6

2. C.B. Wei, X.B. Tian, S.Q. Yang, X.B. Wang, Ricky K.Y. Fu, Paul K. Chu, Anode current effects in plasma electrolytic oxidation, Surface and Coatings Technology, Volume 201, Issues 9–11, 2007, Pages 5021-5024.

3. Bin Li, Jing Xue, Chao Han, Na Liu, Kaixuan Ma, Ruochen Zhang, Xianwen Wu, Lei Dai, Ling Wang, Zhangxing He, A hafnium oxide-coated dendrite-free zinc anode for rechargeable aqueous zinc-ion batteries, Journal of Colloid and Interface Science, Volume 599, 2021, Pages 467-475

4. L.K Xu, J.D Scantlebury, A study on the deactivation of an IrO2–Ta2O5 coated titanium anode, Corrosion Science, Volume 45, Issue 12, 2003, Pages 2729-2740.

5. Sevidova, E.K., Kononenko, V.I. Assessment of bioengineering ceramic coatings using the wetting method. J. Superhard Mater. **29,** 82–85 (2007). https://doi.org/10.3103/S1063457607020037

6. Pogrebnjak, A.D., Tyurin, Y.N. The structure and properties of Al_2O_3 and Al coatings deposited by microarc oxidation on graphite substrates. Tech. Phys. **49,** 1064–1067 (2004). https://doi.org/10.1134/1.1787669

7. Umanskyi, O., Storozhenko, M., Tarelnyk, V. et al. Electrospark Deposition of Fenicrbsic–Meb_2 Coatings on Steel. Powder Metall Met Ceram **59,** 57–67 (2020). https://doi.org/10.1007/s11106-020-00138-5

8. Markov, M.A., Bykova, A.D., Krasikov, A.V. et al. Formation of Wear- and Corrosion-Resistant Coatings by the Microarc Oxidation of Aluminum. Refract Ind Ceram **59,** 207–214 (2018). https://doi.org/10.1007/s11148-018-0207-3

9. Gutsalenko, Y.G., Sevidova, E.K. & Stepanova, I.I. Evaluation of Technological Capability to from Dielectric Coatings on AK6 Alloy, Using a Method of Microarc Oxidation. Surf. Engin. Appl.Electrochem. **55,** 602–606 (2019). https://doi.org/10.3103/S1068375519050041

Диха О.В., Бабак О.П., Маковкін О.М., Посонський С.Ф. Трибологічні властивості анодно-іскрових покрить на сплавах алюмінію.

Встановлено, що в теперешній час технологія анодно-іскрових покрить в загальному достатньо добре досліджена. Однак недостатність рекомендацій по вибору режимів технологічних процесів та трибологічних характеристик в різних умовах експлуатації обмежують широке впровадження даної технології. Задачею даної роботи був аналіз процесів нанесення анодно-іскрових покрить, вдосконалення технології та дослідження зносостійкості зразків, оброблених за вказаною і традиційною анодною технологією. Розробка технології нанесення захисних покриттів на вентильні метали в умовах іскрового розряду включала в себе вибір електроліту і режиму роботи ванни: напруга, густина струму, гідродинамічні умови та інші параметри. Випробування на зносостійкість проводилися на спеціальній установці. Конструктивно установка виконана двухпозиційною, що дозволяє одночасно випробувати два зразки з різними умовами навантаження при постійній швидкості ковзання. Конструкція установки реалізує схему тертя вал-вкладиш. Дослідження анодно-іскрових покриттів в режимі граничного змащування досліджувалось у середовищі індустріального масла. За критерій зношування приймався ваговий знос зразків по результатам вимірювань ваги до і після зношування. Встановлено, що тривалий електроліз в умовах іскріння приводить до утворення анодних покриттів, що перевищують за своїми властивостями плівки, отримані шляхом безіскрового оксидування. Порівняльні дослідження зносостійкості анодно-іскрових покрить і гальванічних анодних покрить за одакових умов випробувань показали, що знос анодно-іскрових покрить майже вдвічі нижчий для всього навантажувального діапазону. Розглянута технологія рекомендується для підвищення зносостійкості елементів приладів з алюмінієвих сплавів, що працюють в умовах корозійно-механічного зношування.

Ключьові слова: анодно-іскрові покриття, алюмінієві сплави**,** трибологічні випробування, знос, коефіцієнт тертя