Tribological tests of micro-arc oxidation coatings in environmentally safe lubricants

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Abstract. This study is devoted to wearing resistance of MAO-coatings formed on aluminum alloys 2024 (Al-Cu-Mg) and 7075 (Al-Zn-Mg-Cu) at the friction in pair with steel 100Cr6 in environmentally safe lubricants and represents a generalization and analysis of tests' results. Investigations were conducted using two methods: reciprocating sliding on the “ball-on-disk” friction scheme and unidirectional sliding on the “pin-on-disk” friction scheme. As environmentally lubricants were used some base oils like polyalphaolefin (PAO), polyethylene glycol (PEG), Silicon Oil, perfluorinated polyether (PFPE) and diisotridecyl adipate ether (DITA). Tests on the first friction scheme allowed us to determine the maximal value of load for investigated friction pairs and tests on the second friction scheme showed their antifriction properties in different lubricants and in the mode of the greasing starvation. There was revealed that MAO-coatings formed on alloy 7075 at high contact pressures demonstrate a friction coefficient lower than on alloy 2024. Some problems of the used “pin-on-disk” scheme is discussed also for improving the tests' results data.

1. Introduction
It is known that the lubricants used in friction units have a great influence on their tribological behavior. Properly selected materials can reduce the wear rate by tens or hundreds of times, compared with the same processes at the absence of lubrication. Currently, environmental challenges occupy the main place and include such issues as reduction of energy, resources, and emissions. In this regard, lubricants attract more and more attention from the public.

Since the influence of lubricants on the biosphere and humanity is very diverse, determined by many factors and manifests itself at all stages - from production to recycling of secondary raw materials, the solution is to develop and use environmentally friendly lubricants.

On the other hand, the development of new ecologically safe technologies for material treatment can be the other way contributed to the high wear resistance of the material. One such promising technology is the micro-arc oxidation method [1-5].

Micro-arc oxidation (MAO) is a relatively new and perspective type of metallic alloys electrochemical treatment, which originates from traditional anodizing. The distinctive feature of MAO is surface micro-discharges participating in the process, which have a significant and specific influence on phases and structures formation [6]. As a result, structure and composition of oxide layers
significantly different and properties much improved than at anodizing. Another feature of micro-arc oxidation is the fact that forming of oxide coating in this method can take place in both directions relative to the initially nominal surface (but with different speeds) [7,8]. For example, the accretion of coating thickness in one µm can contribute a respective layer modification depth of two µm. Thus, the micro-arc oxidation traits two different types of modification methods at the same time:

- by application of coatings (i.e. modification with the thickness growth);
- by changing of state, structure, properties of surface and near-surface (i.e. modification without thickness growth).

There are some main advantages of micro-arc oxidation:

- possibility of obtaining coatings with a wide range of properties such as wear, corrosion and erosion resistance, etc.
- wide range of coating thicknesses;
- high adhesion of the coating to substrate;
- absence of necessity of preliminary preparation the surface at the beginning of the technological chain;
- well developed technology for valve metals and alloys;
- environmental friendliness.

Disadvantages of the method are:

- difficulties of forming MAO coating for ferrous alloys;
- the problem with uneven coating thickness on parts of complex shape;
- relatively high energy consumption.

MAO-coatings find a scope of application in different braches of industry such as mechanical engineering, aerospace industry, oil and gas, medicine etc. Nowadays application of micro-arc oxidation become wider.

The goal of the presented work is investigation of tribotechnical performance of micro-arc oxidation coatings in environmentally safe lubricants.

2. Materials and methods

Micro-arc oxidation coatings were formed on samples of aluminum alloys 2024 (Al-Cu-Mg) and 7075 (Al-Zn-Mg-Cu). For the coatings’ formation on these samples, two types of weakly alkaline electrolytes were used (electrolyte №1 and №2 in further). The porosity of coatings was measured on micro-sections using method of texture image analysis. In addition, coatings thickness was measured using eddy current thickness gauge.

As lubricants were used base oils such as polyalphaolefin (PAO), polyethylene glycol (PEG), Silicon Oil, perfluorinated polyether (PFPE) and disotridecyl adipate ether (DITA) [9,10]. Oils were selected so that they had approximately equal physical properties like kinematic viscosity at 40 °C - 25 mm²/s (25 cSt). Physical properties of used base oils are presented in table 1.

| Name of oil | n(25°C), mm²/s | n(40°C), mm²/s | n(100°C), mm²/s |
|-------------|----------------|---------------|-----------------|
| PFPE        | 54,233         | 27,215        | 4,6164          |
| DITA        | 49,397         | 25,802        | 5,2149          |
| PAO         | 48,122         | 26,010        | 5,2125          |
| Silicon Oil | 51,026         | 38,774        | 16,108          |
| PEG         | 44,012         | 22,452        | 4,1474          |

The friction tests were conducted under two contact conditions: reciprocating sliding using a “ball-on-disk” friction scheme and unidirectional sliding on a “pin-on-disk” friction scheme. Friction coefficient, volume and mass loss on the MAO-coated aluminum alloys were also determined.
The “ball-on-disc” friction scheme tests were performed using balls with a diameter 10 mm from steel 100Cr6 and discs Ø24x8 mm treated by MAO-method. In the table 2 are presented the average values of coating thickness and porosity.

Table 2. “Ball-on-disc” scheme. Average values of coating thickness and porosity.

| Electrolyte | Average coating thickness, μm | Average porosity, % |
|-------------|-------------------------------|---------------------|
|             | 2024                          | 7075                |
| №1          | 84                            | 150                 |
| №2          | 77                            | 127                 |

The tests were carried out using the SRV3 tribometer, which realizes the “ball-on-disc” scheme. Investigations were conducted into two stages: with increasing load and at the constant load. At the tests with increasing load following parameters were used: oscillation frequency 50 Hz, stroke 1 mm, temperature 40 °C, and the load had been increasing on 25N from 400N to 600N every 7 minutes, duration of test 80 minutes.

According to the results with increasing load tests, better samples of lubricants were taken for the next stage with constant load tests.

The duration and load had not been changing in experiments with the constant load. The test time was 60 minutes, and the loads were 400N and 600N.

As samples for the tests according to the “pin-on-disc” scheme, there were used pins with MAO-coatings Ø10x8 and the disc with diameter 110 mm made from steel 100Cr6. The tests were conducted on the tribometer of the own design of Gubkin University [11]. The working part of this tribometer is presented in figure 1.

Figure 1. The working scheme of tribometer: 1 – rotating steel disk; 2 – fixed sample with MAO-coating.

Performing studies, the following parameters were used: load 200 N; disk rotation speed 38 rpm; duration of 60 minutes; two types of tests: with lubricant in contact and with grease remained in the pores (the emergency mode – greasing starvation). In the Table 3 are presented the average values of coating thickness and porosity for these tests.

Table 3. “Ball-on-disc” scheme. Average values of coating thickness and porosity.

| Electrolyte | Average coating thickness, μm | Average porosity, % |
|-------------|-------------------------------|---------------------|
|             | 2024                          | 7075                |
| №1          | 100                           | 150                 |
| №2          | 127                           |                     |

Tests’ data on the friction pattern "ball- on-disk" was the basis for the selection of lubricants for the friction scheme "pin-on-disk." From all investigated environmentally oils [12] for further tests only
PEG, PAO and DITA oils were selected. In addition, the composition of lubricants was expanded by the addition of the additive. Zinc dithiophosphate (ZDDF) [13] - anti-wear additive was added to each oil in an amount of 1600 ppm (0,16%).

3. Results and discussion

3.1. “Ball-on-disc” tests

3.1.1. “Ball-on-disc” with increasing load. The test results according to the scheme “ball-on-disc” with increasing load are presented in figure 2.

![Figure 2](image)

Figure 2. “Ball-on-disc”. Tests with increasing load. (a) Average values of the friction coefficients; (b) Average volume wear.

The results performing lower friction coefficient of samples with MAO-coating on alloy 7075, in comparison with the alloy 2024 (except for tests samples from 7075 alloy in PAO). It is also necessary to note a significant decrease in the wear of the MAO-coatings formed on the alloy 7075 during friction in PAO oil, while the MAO-coatings on the 2024 alloy had destruction up to the substrate.

3.1.2. “Ball-on-disc” with constant load. The test results according to the scheme “ball-on-disc” with constant load are presented in figure 3.

![Figure 3](image)

Figure 3. “Ball-on-disc”. Tests with constant load. (a) Average friction coefficient at 400N; (b) Average friction coefficient at 600N.
PEG oil at the load of 400 N and with coatings formed in the first electrolyte on 2024 alloy showed the best result, but the coatings formed in the second electrolyte performed worse. DITA oil at 400 N showed an approximately equal coefficient of friction with all compositions of electrolytes and coatings. At the load of 600 N, the friction coefficient for samples formed on the alloy 7075 is approximately the same as at the load of 400 N. MAO coatings on the alloy 2024 at this load demonstrate an increase of friction coefficient.

3.2. “Pin-on-disc” tests
The test results according to the “pin-on-disk” scheme with lubricant are presented in figure 4.

Figure 4. “Pin-on-disc” tests with lubricants. (a) Average friction coefficient; (b) Average mass wear.

In this case, a low friction coefficient was observed for samples with MAO-coatings formed on the alloy 7075 with the lubricant of PEG + ZDDP oils. In general, coatings on alloy 7075 have a friction coefficient lower than the same on alloy 2024, however, in some cases, the friction coefficient excess was observed. MAO-coatings on the alloy 7075 after testing showed a mass increase.

Figure 5 provides the results of tests in emergency mode.

Figure 5. “Pin-on-disc” emergency tests. (a) Average friction coefficient; (b) Average mass wear.
Under such conditions, low friction coefficients demonstrate the MAO-coatings in PAO oil and its mixture with ZDDP. In general, a high friction coefficient was observed for coatings based on alloy 7075, while at the same time they had lower mass wear. The main problem with the “pin-on-disc” tests was the increase of the final mass when tested with a lubricant. There were two ideas about the origin of this phenomenon. Firstly, the accumulation of excess oil in the pores of the coating and, as a consequence, the growth of mass. Secondly, the “sticking” or transfer of the material of the counter body over the MAO-coating. However, in the first case, the same tests procedure and low porosity of coatings on alloy 7075 relative to the same on alloy 2024 allowed disregarding the assumption about oil accumulation in pores. To verify the possibility of transfer of steel to the MAO-coating surface, there were made attempts to search for sticking zones using a scanning electron microscope (SEM). But, according to the results of SEM-microscopy research, the presence of steel particles was not discovered on the MAO-coating surface.

4. Conclusions
To sum up, the mentioned above the following conclusions can be drawn, such as, MAO-coatings formed on alloy 7075 after “ball-on-disk” (high contact pressure) tests demonstrate friction coefficient less than the coatings on alloy 2024. MAO-coatings on alloy 7075 had less wear at any of the test schemes. Indirectly, can be concluded that the substrate influences the tribotechnical performance of MAO-coatings due to the differences in mechanical properties of 2024 and 7075 alloys. However, it should be researched more in detail: a wider range of applied alloys, contact types, etc. And finally, since within the framework of the “pin-on-disc” test scheme, there were used relatively small values of loads (not more than 200 N), then the test method should be modified. For instance, some changes must be introduced into the “pin-on-disc” tribometer to increase its range of load.

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