

Fabrication and Triboengineering Properties of Aluminum Composite Ceramic Coatings



A. N. Bolotov, V. V. Novikov and O. O. Novikova

Abstract The paper presents the basics of the technology for fabrication of solid lubricant composite ceramic coatings that are basically a ceramic matrix with antifriction fillers based on magnetite, graphite, and molybdenum disulfide, which are formed on the aluminum alloy using the micro-arc oxidation method. It also shows the features of electrophoretic implantation of dispersed particles of magnetite, graphite, and molybdenum disulfide into a ceramic matrix. The authors have experimentally studied the dependence of coating triboengineering properties on the concentration of solid lubricant particles in the electrolyte and temperature conditions in the friction zone. As a result, they have formed the requirements for the composition of the electrolyte used to apply these coatings. The comparative triboengineering tests have shown that synthesized solid lubricating composite ceramic coatings with antifriction fillers have higher antifriction characteristics, a lower friction coefficient, and are more wear resistant compared to unsupported ceramic materials obtained by a traditional technology of anodic spark oxidation. The new synthesized coatings can improve antifriction characteristics of friction surfaces for units operating in the absence of a lubricant by several times. The wear analysis of the obtained coatings has shown that the obtained ceramic coating with the molybdenum disulfide as a filler has the highest antifriction properties. The triboengineering tests of molybdenum disulfide coatings (as a solid lubricant) confirmed the need for the adsorbed protective films on the dispersed phase particle surface during the microarray application of these coatings to improve antifriction properties of the particles.

Keywords Micro-arc oxidation · Solid lubricant · Ceramic coating · Antifriction filler · Friction · Wear

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1 Introduction

Due to high specific strength, low density, and corrosive resistance, aluminum and its alloys are widely used as an engineering material in engineering and medical industry [1–3]. Their low wear resistance holds the use of aluminum alloys in friction units back. Specialists pay much attention to studying wear resistance of aluminum alloys. However, the analysis of the latest studies shows that traditional methods of improving wear resistance of aluminum products are ineffective.

A promising method for improving the surface properties of aluminum alloys that are important for friction is to create a protective oxide layer on its surface by the micro-arc oxidation method [4–7]. This method assumes that when high-density current passes through the valve metal–electrolyte interface, it creates the conditions for micro plasma discharges to occur on the metal surface in micro volumes with high local temperatures and pressures. The electrochemical action of discharges forms the surface layer consisting of the oxidated forms of base metal elements and electrolyte components [8, 9]. Depending on the micro-arc oxidation mode and electrolyte composition, it is possible to obtain ceramic coatings with a wide range of physico-mechanical properties [10–13]. The structure of the coating obtained by micro-arc oxidation is porous ceramics with a complex composition, which is formed due to metal surface oxidation and inclusion of electrolyte elements in the coating composition. The studies in this field made it possible to obtain oxide layers with a thickness of several hundred micrometers on aluminum. However, that coatings properties were not optimized for friction conditions without a liquid or plastic lubricant (“dry” friction) [14]. At the same time, self-lubricating materials in friction units are in demand in various modern assemblies of machines and mechanisms.

Micro-arc oxidation coatings obtained in suspension electrolytes have a wider range of physico-mechanical properties [15]. In order to obtain solid ceramic coatings, we propose to include micro- and nano-sized particles of an antifriction filler into an oxide matrix. A similar approach allowed obtaining oxide composite coatings with unique abrasive properties [16–18].

1.1 Work Objective

The work objective is to develop some basics of the technology for fabrication of solid lubricant composite coatings, which are ceramic matrix with antifriction fillers based on magnetite, graphite, and molybdenum disulfide formed by the method of micro-arc oxidation on aluminum alloy. To study the antifriction characteristics of the obtained oxide composite coatings by experiment.

1.2 Methodical Issues of Experimental Research

The base material for the study is D1 aluminum-based alloy, which is widely used in engineering (about 4% copper, less than 1% iron, silicon, and manganese). We conducted the synthesis of oxide coatings with antifriction powders in electrolytes containing dispersed solid lubricant materials as a filler. These materials have modified the structure of the hardened surface layer when oxidized.

The installation for the synthesis of coating micro-arc oxidation consisted of a condenser current source of and a bath with a cooling jacket filled with an experimental electrolyte. The electrolyte consists of alkali (NaOH), liquid glass, and the main component—distilled water.

The nanodispersed phase of the ceramic coating was a magnetite that is able to improve mechanical properties of the coatings and reduce friction by reducing adhesive bonds between contacting surfaces. Highly dispersed magnetite (a typical size is about 7 nm) has been obtained by chemical precipitation [16, 19]. The peptization process in a liquid glass solution was carried out in order to protect highly dispersed magnetite particles from oxidation and to prevent their coagulation.

An antifriction coating dispersed phase (in addition to a magnetite), we used finely dispersed graphite and molybdenum disulfide powders (with 2–10 μm particle size) that have high antifriction properties. A surfactant to modify a particle surface was glycerin.

During oxidation, dispersed particles were placed into the coating composition through the arc electrophoresis. Electrolyte particles have been transported to the processed alloy surface by a inhomogeneous electric field, entered the spark discharge burning zone and are included into the coating composition.

We used an MTP friction machine [20] to conduct triboengineering tests of composite coatings in the field of medium pressures. The friction scheme is the following: disk-finger (coated). The counter body materials for testing the obtained antifriction coatings were U8A tool steel and KhVG hardened alloy tool steel (45–50 HRC). An inductive indicator continuously was recording linear wear values. During the research, a sliding speed was 0.15–0.95 m/s and contact pressures were 0.5–15 MPa without using any additional lubricant. The measurement error for the linear wear intensity did not exceed 17%, for the friction coefficient did not exceed 10%.

The thickness of non-conductive coatings has been determined using an eddy current thickness gauge.

2 A Background Technology for Coating Production

The background technology for producing composite coatings is based on the existing technology of oxide coating micro-arc synthesis on an aluminum alloy [4]. The known coatings obtained in an electrolyte that contains alkali and a sodium

silicate has a sufficient thickness for practical use (up to 0.3 mm), good adhesion with the substrate material, and high hardness. The main disadvantage of the base coating is a high coefficient of dry friction that causes friction pair jamming and quick fatigue failure of contacting surfaces with a high probability. Considering this disadvantage, we modified the coating to reduce the friction coefficient without using a lubricant.

We have solved the problem using electrophoretic injection of solid lubricant particles into the ceramic matrix of the coating. Energizing leads to the growing barrier oxide layer on the surface of the coated aluminum sample, which forms a refractory ceramic matrix. At the same time, in the electrolyte solution, fine solid lubricant particles drop out and are kept by electromagnetic forces on the sample surface. They are gradually placed into the matrix.

However, the inclusion of graphite particles into the coating is complicated due to its good conductive properties. When electrical current is connected, graphite particles subside on the coated workpiece surface and cause its corrosion. They disturb the passive surface layer. Therefore, sites of non-discharge current flow appear.

In order to solve this problem, there are two approaches to form a coating. According to the first approach, the electrochemical process of coating production is divided into two stages. At the first stage, a sample is coated in the electrolyte without graphite particles during 15 min under the voltage of 450–500 V. It is sufficient to create a thin dielectric coating of 3–10 μm . Further, the process is carried out in the electrolyte containing graphite particles with an end-point voltage of 500–600 V and current density of 3 A/dm^2 during 1 or more hours. Hydrophobized graphite particles in the suspension electrolyte can coagulate and subside, which lowers their concentration in the coating. In order to avoid conglomerates, the electrolyte is actively stirred using compressed air barbotage. The obtained ceramic coating has a concentration gradient of a dispersed graphite filler, which is absent in the layer bordering aluminum.

A distinguishing feature of the second method of forming a coating is the fact that graphite is coated by a dielectric layer from glycerin adsorbed on its surface in order to decrease electrical conductivity of the contact graphite—aluminum surface. To prevent glycerin decomposition and changing its properties as a polar liquid at high temperatures, the electrolyte is cooled to a temperature of 5–10 $^{\circ}\text{C}$. Figure 1 shows the coating microstructure (black dots represent inclusions of graphite particles).

Another material of the dispersed phase is a molybdenum disulfide MoS_2 . It has good lubricating properties. Additionally, it is a dielectric according to its electro-physical features. A disadvantage of molybdenum disulfide is its relatively low chemical stability. During coating synthesis, due to high temperature and oxidizing environment, it can turn into molybdenum dioxide and trioxide that do not have solid lubricant properties. In order to prevent oxidation of molybdenum disulfide, we also used the protective properties of glycerin adsorbed on the particles. The electrochemical coating process included initial voltage of 470 V and final one of 580 V, the current density of 2.4 A/dm^2 , and it lasted for several hours.

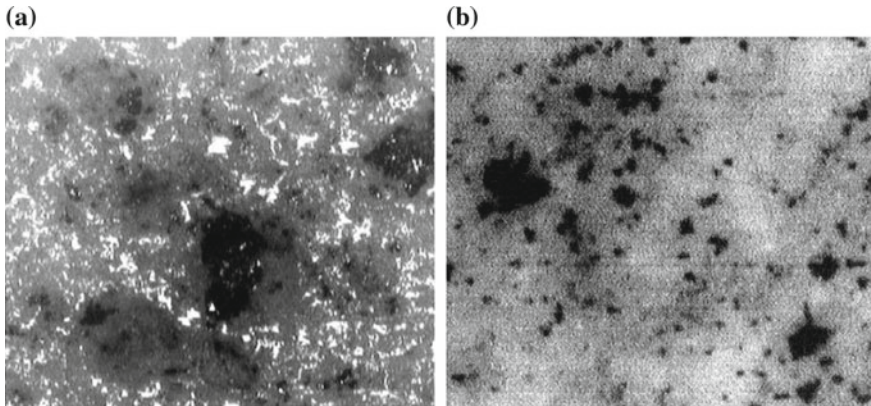


Fig. 1 Surface microstructure of the ceramic composite coating with a graphite filler on D1 aluminum alloy: **a** in typical light; **b** in polarized light ($\times 500$)

The introduction of nano dispersed magnetite particles into the composite coating composition did not cause any technological difficulties and did not significantly affect the micro-arc oxidation process.

The base distilled water electrolyte contains 0.1%wt of NaOH alkali and 1.1%wt of sodium silicate (the suspension electrolyte with MoS₂ contains 1.5%wt of sodium silicate). We also added dispersed particles of graphite, molybdenum disulfide, and magnetite to the base electrolyte (2–6%wt).

3 The Results of Experimental Studies and Their Discussion

It is established that the friction coefficient of a ceramic coating with a dispersed filler MoS₂, which is not treated in glycerin, is 0.25–0.3. This is typical for coating micro-arc oxidation without antifriction fillers. This confirms that it is reasonable to use glycerin or a surfactant with similar ionic properties.

Figure 2 shows time dependences of the friction coefficient for the studied materials. Test conditions are the following: the contact pressure is 1.5 MPa and the sliding speed is 0.47 m/s. At the beginning of the test, there is running in of coating materials, therefore the friction force decreases. The friction coefficient increases due to the gradual abrasion of coatings and the appearance of metal contact areas. The friction force value for composite coatings with a molybdenum disulfide is lower than the one of coatings with dispersed graphite (curves 2 and 3) at permissible operating temperatures of the friction unit not above than 150 °C.

Figures 3 show the effect of the concentration in an antifriction filler electrolyte on triboengineering properties of ceramic coatings. The increase in the concentration of MoS₂ particles and graphite leads to an almost linear decrease of the friction

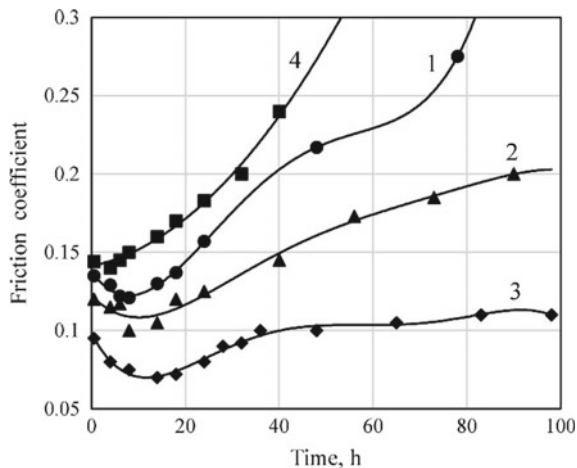


Fig. 2 Friction coefficients of composite ceramic coatings depending on test duration. Antifriction fillers: 1—no filler, 2—graphite, 3—molybdenum disulfide, and 4—magnetite

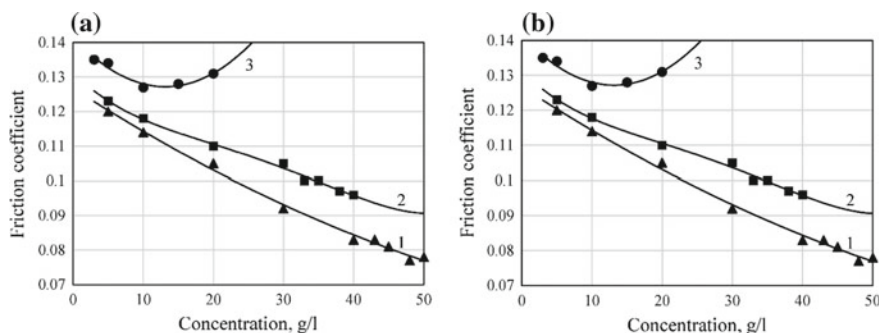


Fig. 3 Dependence on MoS₂ particle concentration (1), graphite (2), and magnetite (3) in the electrolyte: **a** friction coefficient; **b** linear wear intensity

coefficient (Fig. 3a). The dependence of the linear wear intensity on MoS₂ concentrations (Fig. 3b, curve 1) is extreme. The optimal concentration of MoS₂ in the electrolyte is about 45 g/l, which provides about 25%vol of MoS₂ concentration in the formed coating. Further increase in the concentration of molybdenum particles in the electrolyte (over 50 g/l) and in the finished coating leads to a decrease in its strength, wear resistance, and degradation of adhesive properties of adhesion with a substrate material.

Graphite lubricating properties in air are lower than those of MoS₂. Considering this fact, increasing its concentration in the electrolyte leads to a less significant decrease in the friction coefficient. The optimal concentration is 30 g/l in the electrolyte and, consequently, about 20% in the coating composite material.

Table 1 Properties of composite coatings with various antifriction fillers

Dispersed phase	Friction coefficient	Linear wear rate	Coating hardness (GPa)	Oxide layer thickness (mm)
Molybdenum disulfide	0.07–0.11	5×10^{-9}	10–12	0.1–0.50
Graphite	0.10–0.16	7×10^{-9}	12–14	0.1–0.45
Magnetite	0.15–0.26	9×10^{-9}	14–17	0.1–0.30
No filler	0.11–0.25	15×10^{-9}	12–14	0.1–0.40

The critical concentration value is defined as 35 g/l (Fig. 3b, curve 2). Above this value, there is a sharp increase in the linear wear intensity due to a decrease in coating thickness and its discontinuity. A further increase in the concentration of graphite particles in the electrolyte to 40 g/l leads to breaking the coating formation process due to the catastrophic growth of corrosion spots on the composite sample surface.

Table 1 presents the results of triboengineering tests of the obtained coatings. It also considers the properties of coatings without fillers. The data in the table shows that the inclusion of nano dispersed magnetite particles into the coating composition increases coating micro hardness. This is due to the fact that the coating becomes less loose as porosity decreases by twice. Frictional properties of magnetite coatings have improved under unlubricated friction. However, their overall level is lower than the level of coatings with solid lubricants.

Figure 4 presents photographs of friction tracks on the coating with MoS₂ particles. Dark areas on the friction surface of a ceramic antifriction coating sample and a steel counter sample indicate the formation of a protective MoS₂ lubricating film on them.

We have studied how contact pressure affects the linear wear intensity of coatings with graphite and molybdenum disulfide particles. The ceramic coating with the MoS₂ filler has shown the highest antifriction characteristics in the entire range of working pressures (0.5–7 MPa).

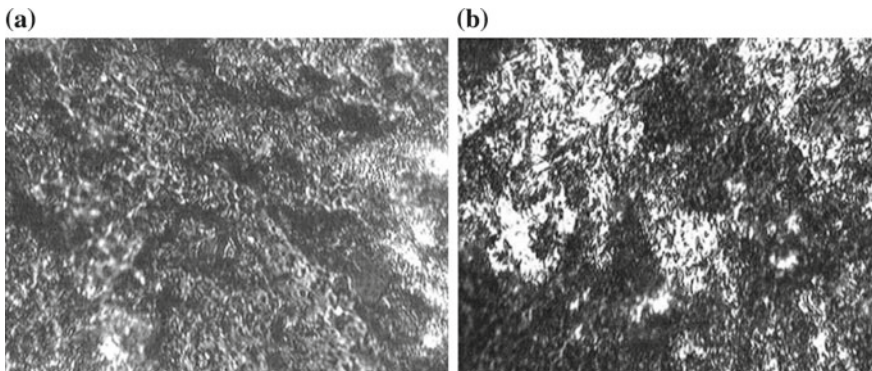


Fig. 4 Composite coating friction surfaces with molybdenum disulfide: **a** A coating surface; **b** A counter body (KhVG steel)

The increased temperature in the friction zone significantly affects coatings with molybdenum disulfide and to a lesser extent on the coating with graphite. At temperatures up to 150 °C, coatings with molybdenum disulfide particles show better triboengineering properties than coatings with graphite particles, while at temperatures of 200–450 °C coatings with graphite particles have some advantages due to different thermal stability of dispersed phase particles and a different lubricating mechanism.

In real friction units, we can often see counter body material heavy wear, not an antifriction material. In the above-mentioned experiments, the steel counter body wear was of the same order as the coating wear. The higher its hardness, the smaller it was.

Triboengineering studies have confirmed the effectiveness of dispersed solid lubricants in the synthesis of ceramic coatings used in dry friction units. They have also shown the feasibility of using surfactants (glycerin) to produce coatings.

4 Conclusion

We propose a new approach to fabrication of solid lubricant composite ceramic coatings on aluminum and its alloys using micro-arc oxidation. The method assumes the additional injection of a finely dispersed molybdenum disulfide, which is modified by a surfactant, into an electrolyte.

It is shown that oxide ceramic coatings obtained by micro-arc oxidation have higher antifriction and antiwear properties. Therefore, they are suitable to apply in slide bearings without additional lubrication with liquid or consistent materials. A composite ceramic coating with a solid lubricant filler MoS₂ has a linear wear rate and a friction coefficient 1.5–2 times lower than a coating with dispersed graphite particles. Oxide coatings with a nano dispersed magnetite have substantially better triboengineering characteristics than traditional aluminum oxide coatings have. However, they are not as good as ceramic solid lubricants filled with MoS₂.

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