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Tribological properties of Al₂O₃ layers after thermo-chemical treatment

Mateusz Niedźwiedź^{1*}, Władysław Skoneczny¹, Marek Bara¹, Vladimír Bulej²

¹Institute of Materials Engineering, Faculty of Science and Technology, University of Silesia in Katowice, 75 Pułku Piechoty 1a, 41-500 Chorzów, Poland

²Department of Automation and Production Systems, Faculty of Mechanical Engineering, University of Žilina, Univerzitná 8215/1, 010 26 Žilina, Slovakia

*Corresponding author: Mateusz Niedźwiedź (mateusz.niedzwiedz@us.edu.pl)

ABSTRACT

The article presents the influence of the thermo-chemical treatment of Al₂O₃ layers on their tribological properties. The Al₂O₃ layers were produced on the EN AW-5251 aluminium alloy by means of direct current anodizing in a three-component electrolyte. For the sake of comparison, some of the samples were thermochemically treated in three liquids (sodium sulphate solution, sodium dichromate solution, distilled water). The parameters of the production and thermo-chemical treatment were selected on the basis of two Hartley's plans. The tribological properties were determined on the basis of a tribological test carried out for a pin-on-disc friction pair on a T-17 tester in reciprocating motion. The tests were carried out in conditions of technically dry friction. Thanks to the tests, coefficient of friction μ and the mass wear, together with the intensity of the material wear were determined. The use of thermo-chemical treatment in the sodium dichromate solution contributed to an increase in coefficient of friction μ and a reduction in the wear intensity of the polymer from 36 $\mu\text{g}/\text{km}$ (layer without thermo-chemical treatment) to 21.33 $\mu\text{g}/\text{km}$ (layer after thermo-chemical treatment in the sodium dichromate solution). The conducted stereometric tests before and after the tribological test for selected samples allow the authors to state that the thermo-chemical treatment in the sodium dichromate solution increases the amplitude parameters of surface roughness. The study of the surface morphology of the layer with the lowest mass wear showed the formation of an additional sub-layer as a result of thermo-chemical treatment carried out in the sodium dichromate solution.

Keywords: Al₂O₃ layers; thermo-chemical treatment; tribological properties; coefficient of friction; mass wear.

1. Introduction

Contemporary times require the use of materials with a high strength-to-weight ratio and environmentally friendly materials (easy to recycle without loss of their properties). Aluminium is a material that meets the above requirements; therefore, it is widely used in technology [1]. Pure aluminium is characterized by a low absolute strength and a low melting point; thus, in order to improve its mechanical properties, aluminium is combined with elements to obtain durable alloys [2]. In order to protect aluminium against corrosion and increase its mechanical strength, the so-called Al₂O₃ (oxide) layer is produced on the aluminium surface by one of the electrochemical processes - anodizing, [3-4]. The produced oxide layer has a thickness of a few to several micrometres and is characterized by a several times higher hardness than pure aluminium [5]. An extremely important property of Al₂O₃ layers is their high abrasion resistance, which allows them to be used in machines and devices in sliding contacts [6]. The durability and reliability of machines and devices is most often determined by testing the moving friction pairs

(sliding or rolling), which are the weakest links. The machine or device owes its failure-free operation in certain frictional conditions to the appropriate selection of cooperating materials, together with the correct design solution. The failure-free operation of machines also means not exceeding the maximum values of the permissible operating parameters. For this to be possible, it is necessary to know the properties of the materials used in the sliding contacts, especially the tribological properties. The experimental route allows detailed data to be determined on the course of the friction process and material wear as a result of sliding contacts [7-11]. The oxide layers used in kinematic sliding pairs are suitable for interaction with metals and ceramics (limited lubrication) and with plastics (technically dry friction). A very important element that determines tribological cooperation is the formation of a technically dry lubricating layer between the cooperating elements in the case of friction. It contributes to a significant reduction of friction, which results in lower wear of the cooperating elements [12].

The cooperation of Al₂O₃ layers under conditions of technically dry friction should be carried out using plastics

Table 1. Chemical composition of EN AW-5251 aluminium alloy

Chemical composition according to manufacturer's test in [%]								
Mg	Mn	Si	Fe	Cu	Zn	Cr	Ti	Al
1.9	0.26	0.20	0.32	0.05	0.01	0.02	0.02	97.2

exhibiting film-forming properties, which include plastics with a dispersion phase in the form of graphite, PTFE, or MoS₂ [13-15]. Currently, the most widely used materials in the sliding elements of industrial devices and machines those are containing PTFE (polytetrafluoroethylene), which is characterized by a very low coefficient of friction. Unfortunately, pure PTFE has several significant disadvantages such as low hardness, poor thermal conductivity, and load creep. In order to eliminate or minimize these disadvantages, plastics containing PTFE only as a lubricant have been developed, examples of which are TG15, PEEK/BG, T5W, and T7W. Lubrication-free contacts require oxides of low roughness and surface porosity. The main purpose of hard Al₂O₃ layers is to work with materials possessing properties for creating a sliding film. The presence of the film significantly changes the type of cooperation from material/oxide layer to material/material [16].

In order to verify the sliding properties of the created oxide layer during operation in the device in which it will be applied, so-called tribological tests are previously carried out. The actual operating conditions of the friction contact are mapped such as the speed of movement, unit pressures, contact geometry, kinematics and dynamics of load, overlap value, and lubrication. Tribological tests are conducted both in laboratory and operating conditions. Laboratory tests enable detailed analysis of the physical phenomena of wear and friction and are comparable to the actual operating conditions of machines. The condition of the surface layer of the material is very important in terms of durability and reliability of the cooperating machine elements. The reason for this state of affairs is the action of processes and phenomena that occur during friction [17]. Al₂O₃ layers produced with the hard-anodizing method are characterized by very high tribological resistance. Hard

anodizing is distinguished by very versatile possibilities of changing the properties of the oxide layer (surface roughness and morphology). The porosity of the oxide layer is of great importance in terms of maintaining the lubricating material during tribological cooperation. More specifically, high porosity allows the formation of a highly durable sliding film on the surface of the layer (cooperation with the polymer) and plays an important role in lubricant retention (cooperation with limited lubrication).

Many researchers have carried out tribological tests of Al₂O₃ layers produced by different methods and using various modifications. Publication [18] should be cited, in which the authors compared the tribological properties of the oxide layers before and after the modification of IF-WS₂. The layers were produced at a constant current density of 3 A/dm² for 60 minutes in a ternary electrolyte at the temperature of 303 K. The modification of IF-WS₂ was performed with methanol and ethylene glycol. Tribological tests were conducted with the TG15 polymer using sliding contact. A higher coefficient of friction and wear intensity were demonstrated for the unmodified IF-WS₂ layers. In subsequent studies [19], the researchers conducted tribological tests on graphite-modified Al₂O₃ layers. The layers were produced by hard DC anodizing with an electric charge of 180 A·min in a three-component electrolyte at the constant temperature of 303 K. The layers were modified with duplex technology. PEEK plastic as well as PEEK/BG and T5W composites were used as the tribological partner. It was shown that the modification with graphite significantly lowered the frictional forces and the wear of the plastic and the composites. Publication [20] should also be cited, in which the authors dealt with the production of oxide layers using galvanostatic anodizing using 15% H₂C₂O₄ as electrolyte without or with the addition of H₂C₂O₄, corundum and a 60% PTFE

Table 2. Hartley's plan for layers without thermo-chemical treatment

Sample	Controlled factors					
	On a natural scale			On a standard scale		
	Current density j [A/dm ²]	Electrolyte temperature T [K]	Process time t [min]	x1	x2	x3
01A	2	293	90	-1	-1	1
01B	4	293	30	1	-1	-1
01C	2	303	30	-1	1	-1
01D	4	303	90	1	1	1
01E	2	298	60	-1	0	0
01F	4	298	60	1	0	0
01G	3	293	60	0	-1	0
01H	3	303	60	0	1	0
01I	3	298	30	0	0	-1
01J	3	298	90	0	0	1
01K	3	298	60	0	0	0

Table 3. Hartley's plan for layers with thermo-chemical treatment

Sample	Controlled factors					
	On a natural Scale			On a standard scale		
	Current density j [A/dm ²]	Compound for thermo-chemical treatment (Density) [g/cm ³]	Process time t [min]	x1	x2	x3
02A	2	Water (0.998)	90	-1	-1	1
02B	4	Water (0.998)	30	1	-1	-1
02C	2	Sodium dichromate (2.52)	30	-1	1	-1
02D	4	Sodium dichromate (2.52)	90	1	1	1
02E	2	Sodium sulphate (1.46)	60	-1	0	0
02F	4	Sodium sulphate (1.46)	60	1	0	0
02G	3	Water (0.998)	60	0	-1	0
02H	3	Sodium dichromate (2.52)	60	0	1	0
02I	3	Sodium sulphate (1.46)	30	0	0	-1
02J	3	Sodium sulphate (1.46)	90	0	0	1
02K	3	Sodium sulphate (1.46)	60	0	0	0

suspension. The layer with the best mechanical properties (high hardness, high wear resistance and low coefficient of friction), without structural defects, was produced during anodizing at 283 K at the current density of 1 A/dm² in an electrolyte with the addition of corundum and PTFE. The literature analysis showed a significant lack of research on the influence of the thermo-chemical treatment of Al₂O₃ layers using a sodium dichromate solution, sodium sulphate and distilled water on tribological properties, which makes our research innovative.

The tests performed can be used, for example, in pneumatic actuators where the actuator cylinder can be made of EN AW-5251 aluminum alloy and reinforced with a thermochemically treated Al₂O₃ layer. Sealing rings of the actuator are made of e.g. T7W material, on which the tests were carried out. The reciprocating tester T17 reflects the nature of the actuator's operation.

2. Materials and Methods

2.1. Research Material

The oxide layers were produced on the EN AW-5251 (PA 2) aluminium alloy. This alloy has a high magnesium content and low admixtures of other elements, which facilitates the production of the oxide layer. The characteristic features of the EN AW-5251 aluminium alloy are high plasticity and high corrosion resistance. The producer of the alloy is Light Metals Plant in Kęty, according to the chemical composition which is presented in Table 1.

The anodizing process was carried out in a three-component electrolyte consisting of an aqueous solution of acids: 18% H₂SO₄ (33 ml/l), C₂H₂O₄ (30 g/l) and C₈H₆O₄ (76 g/l). During the anodizing process, the solution was mixed with a mechanical stirrer at the speed of 100 rpm, changing the direction of rotation after every 10 minutes. The anodizing parameters and compounds for the thermo-chemical treatment were selected on the basis of the experimental plans. Hartley's experiment plan based on a

hypercube for three input variables with three variables was used (Tables 2 and 3).

Table 2 presents the values of the input variables on a natural and standardized scale for the layers produced in the anodizing process without thermo-chemical treatment. The input variables were a current density of 2, 3, 4 A/dm², electrolyte temperature of 293, 298, 303 K and process time of 30, 60, 90 min. After the anodizing was completed, the samples were rinsed in distilled water for 60 min.

Table 3 presents the values of the input variables on a natural and standardized scale for the layers produced in the anodizing process together with thermo-chemical treatment. The input variables were a current density of 2, 3, 4 A/dm², process time of 30, 60, 90 minutes and density of the compounds for thermo-chemical treatment with the values of 0.998 g/cm³ for water, 1.46 g/cm³ for sodium sulphate, 2.52 g/cm³ for sodium dichromate. A constant electrolyte temperature of 298K was used for the anodizing.

The thermo-chemical treatment was performed after thorough rinsing of the samples with the formed Al₂O₃ layers in distilled water. The thermo-chemical treatment was carried out in distilled water with a pH ranging from 6 to 7. The second compound used for the thermo-chemical treatment was sodium sulphate. The treatment was carried out in a bath consisting of 200 g of sodium sulphate (Na₂SO₄ 10 H₂O) and 1 l of distilled water; the pH of the bath was between 6 and 7. The last compound was sodium dichromate; the bath for thermo-chemical treatment consisted of 50 g of dichromate sodium (Na₂Cr₂O₇ · 2 H₂O) and 1 l of distilled water; the pH was 8-9. The thermo-chemical treatment temperature for all the compounds was 371 K, and the process time was 60 minutes. After the end of the process, the samples were rinsed in distilled water and allowed to dry.

T7W material was used as the tribopartner for tribological tests in sliding contact. The material is a composite made on the basis of PTFE with a dispersion phase in the form of powdered technical carbon. It is

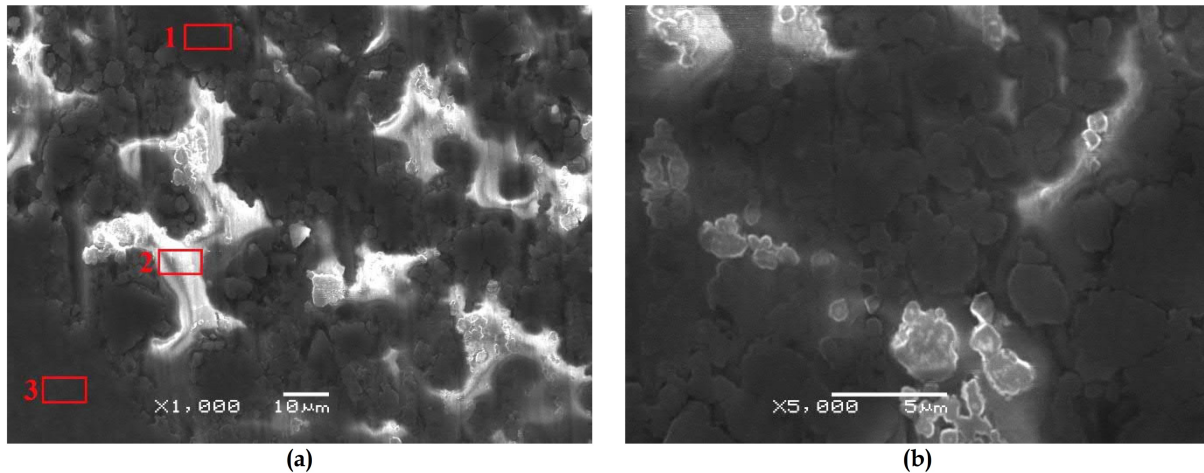


Fig.1. Micrographs of T7W material pin surface: (a) 1,000x magnification used for EDS analysis, (b) 5,000x magnification

widely used in hydraulic and pneumatic systems, in particular in the production of guide rings used in pneumatic cylinders. Figure 1 shows micrographs of the surface of the T7W material pin with a magnification of 1,000x (used for EDS analysis) and 5,000x.

The SEM micrographs show the heterogeneous structure of the material; the PTFE matrix and the dispersive phase in the form of powdered technical carbon (area 1 and 3). Based on the SEM micrographs, the chemical composition of the material was analysed at three marked points in the micrographs (Table 4).

Table 4. Chemical composition of T7W plastic

EDS analysis area number	Atomic content (C)[%]	Atomic content (F)[%]
1	97.49	2.51
2	40.85	59.15
3	98.73	1.27

The dispersion phase of the material has a high percentage of carbon (areas 1 and 3), while the PTFE matrix contains carbon and fluorine (area 2). The use of carbon in the construction of the material is responsible for the increase in mechanical resistance, reduction of abrasive wear and reduction of linear thermal expansion.

2.2. Research Methodology

Tribological tests were carried out for a pin-on-disc friction pair on a T-17 tester in reciprocating motion. The tests were carried out in dry friction conditions, at a constant ambient temperature of 298 ± 1 K and a relative air humidity of 40 ± 10 %. A constant sliding speed of 0.2 m/s was applied and constant unit pressure of 1 MPa were used. The friction distance during the tribological test was 15 km. The friction force was measured with a Spider 8 transducer, which enables the data to be exported to a PC and saved using Catman 4.5 software. The accuracy of the coefficient of friction results from the accuracy of the force transducer, which is 0.02 N, after calculating the accuracy of the coefficient of friction, an accuracy of $\mu = 0.0003125$ was obtained. The research was carried out without

repetitions.

Surface geometrical structure (SGS) tests were performed to determine the roughness parameters and the geometrical structure of the surface before and after the tribological test. The measurements were made by systematic scanning using a Form TalySurf Series 2 50i contact profilographometer. The basic stereometric parameters from the amplitude group were determined. Isometric (3D) visualizations were made before and after the tribological test.

Microscopic examinations were performed using a Hitachi S-4700 scanning electron microscope. Surface morphology micrographs were taken at 50,000x magnification to observe the nanopores. The anodic oxide layers are poorly conductive, so they charge electrically during operation of the electron beam, which contributes to incorrect observation. For proper observation, the layers were sprayed with carbon using a turbomolecular carbon sputtering machine. The carbon layer enables the rebounding electrons to be discharged and carried away during the study.

3. Results and discussion

In order to determine coefficient of friction μ of the Al₂O₃ layers without thermo-chemical treatment and treated, tribological tests were performed on the T-17 tester in reciprocating motion. The wear of the T7W material was also determined as a result of sliding contact during the test. In order to better visualize both coefficient of friction μ and the wear intensity of the T7W material pin, surface (three-dimensional) diagrams were made, showing the dependence of the results on the anodizing parameters and compounds used for thermo-chemical treatment.

Table 5 shows the values of coefficient of friction μ of the contact of the Al₂O₃ layers produced in the anodizing process according to Table 2 (without thermo-chemical treatment) with the T7W polymer pin.

Table 5. Values of coefficient of friction μ of layer contacts without thermo-chemical treatment with T7W pin

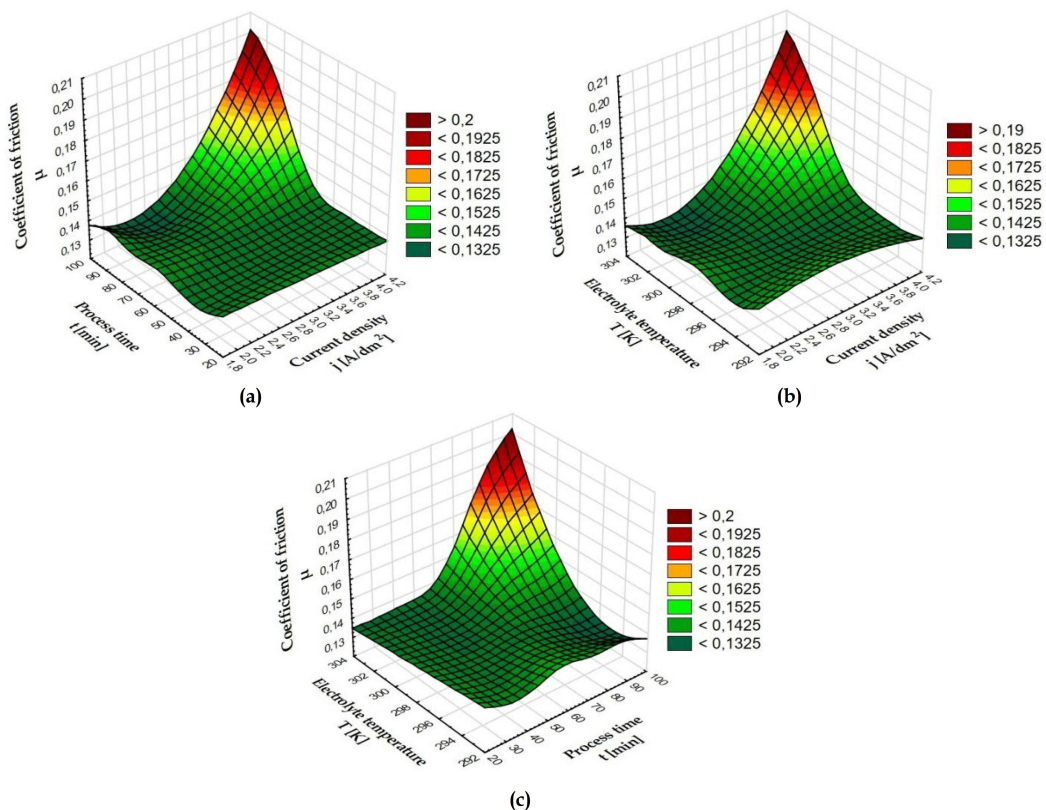
Sample	Coefficient of friction μ
01A	0.138
01B	0.137
01C	0.135
01D	0.182
01E	0.142
01F	0.134
01G	0.145
01H	0.133
01I	0.138
01J	0.132
01K	0.135

The anodizing parameters influence the value of coefficient of friction μ . The highest coefficient of friction was calculated for the contact of the 01D sample produced at the current density of 4 A/dm² for 90 minutes at the electrolyte temperature of 303 K and it was 0.182. The lowest coefficient of friction was calculated for the contact of the 01J sample produced at 3 A/dm² for 90 minutes in the electrolyte at 298 K. However, for the layers produced at the current density of 3 A/dm², the values of the coefficient of friction are very similar to each other.

The influence of the anodizing parameters on the coefficient of friction is shown in Figure 2.

Based on the graphs of the dependence of coefficient of friction μ on the parameters of layer production, it was

Fig.2. Dependence of coefficient of friction μ on: (a) process time and current density, (b) electrolyte temperature and current density, (c) electrolyte temperature and process time



found that high parameters of layer production (current density, electrolyte temperature and process time) significantly increase the coefficient of friction in contact with the T7W polymer. The highest values of the coefficient of friction were observed for the highest production parameters (characteristic elevation in the diagram). The layers produced at the current density of 3 A/dm² are characterized by the lowest coefficient of friction μ , where only slight changes in the value occur between the change in time and temperature of the electrolyte.

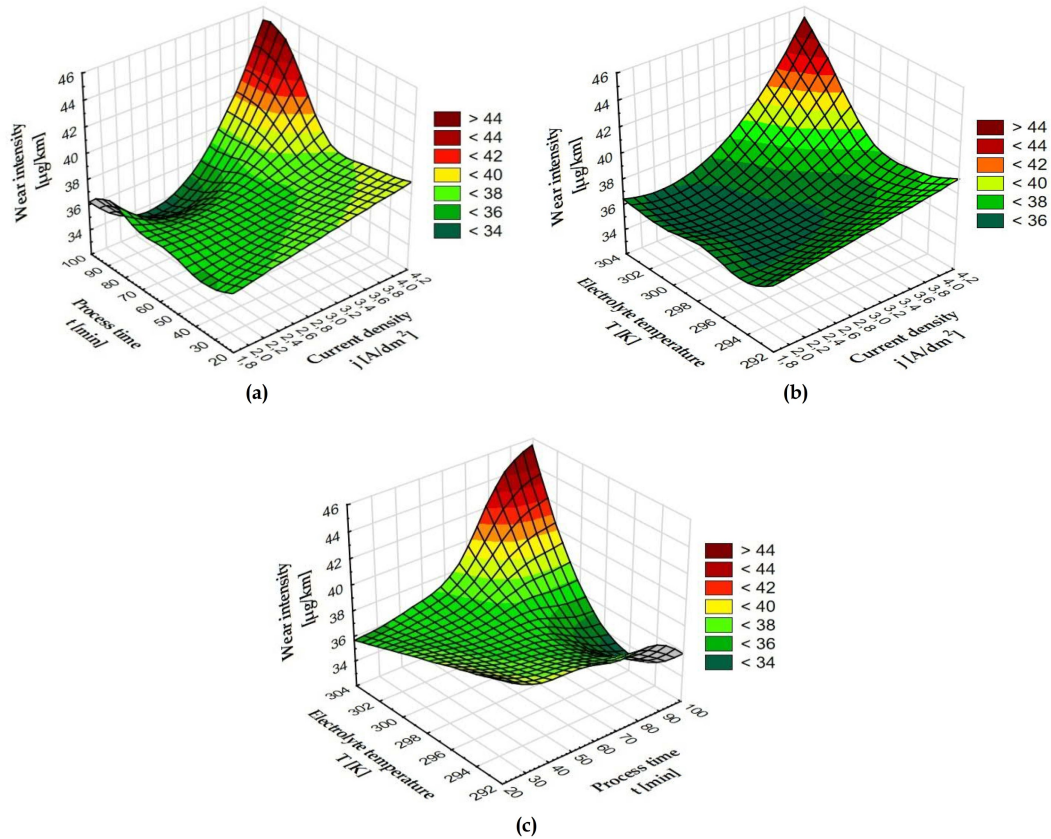
Table 6 shows the values of the mass wear of the T7W polymer pin cooperating with the Al₂O₃ layers produced in the anodizing process according to Table 2 (without thermo-chemical treatment).

Table 6. Mass wear of T7W pin in contact with layers without thermo-chemical treatment

Sample	Mass wear [mg]
01A	0.545
01B	0.575
01C	0.540
01D	0.641
01E	0.551
01F	0.555
01G	0.566
01H	0.548
01I	0.564
01J	0.506
01K	0.540

The anodizing parameters of the layers also significantly affect the mass wear of the material during

Fig.3. Dependence of the wear intensity of T7W pin on: (a) process time and current density, (b) electrolyte temperature and current density, (c) electrolyte temperature and process time



the sliding contact. Sample 01D, produced at the current density of 4 A/dm² for 90 minutes at the electrolyte temperature of 303 K, having the highest coefficient of friction in contact with the polymer, also resulted in the highest material mass wear (0.641 mg). The lowest value of mass wear was measured for the contact of the T7W material and the 01J sample (with the lowest coefficient of friction).

Figure 3 presents three-dimensional graphs showing dependence of the values of the wear intensity on the anodizing parameters.

The analysis of the dependence of the wear intensity of the T7W pin presented in the three-dimensional charts shows that high values of wear intensity occur in the case of sliding contact with a sample produced at high current density (4 A/dm²) with a long process time (Fig. 3a), high temperature electrolyte (303 K) with a long process time (Fig.3b) and a high electrolyte temperature with a long process time (Fig.3c). The lowest value was observed for 3 A/dm², 298 K and 90 minutes (characteristic background refraction in the diagram).

Table 7 presents the values of coefficient of friction μ of the contact of the Al₂O₃ layers produced in the anodizing process according to Table 3 (after thermo-chemical treatment) with the T7W polymer pin.

Table 7. Values of coefficient of friction μ in layer contacts after thermo-chemical treatment with T7W pin

Sample	Coefficient of friction μ
02A	0.145
02B	0.139
02C	0.203
02D	0.227
02E	0.139
02F	0.137
02G	0.144
02H	0.206
02I	0.141
02J	0.147
02K	0.149

The use of the compounds for thermo-chemical treatment significantly influenced the values of coefficient of friction μ . The use of sodium dichromate for thermo-chemical treatment resulted in a significant increase in coefficient of friction μ . The highest value (0.227) was determined for the contact of the pin with sample 02D treated in the sodium dichromate solution. The lowest value (0.137) was determined for the contact of the pin with the 02F sample treated in the sodium sulphate solution.

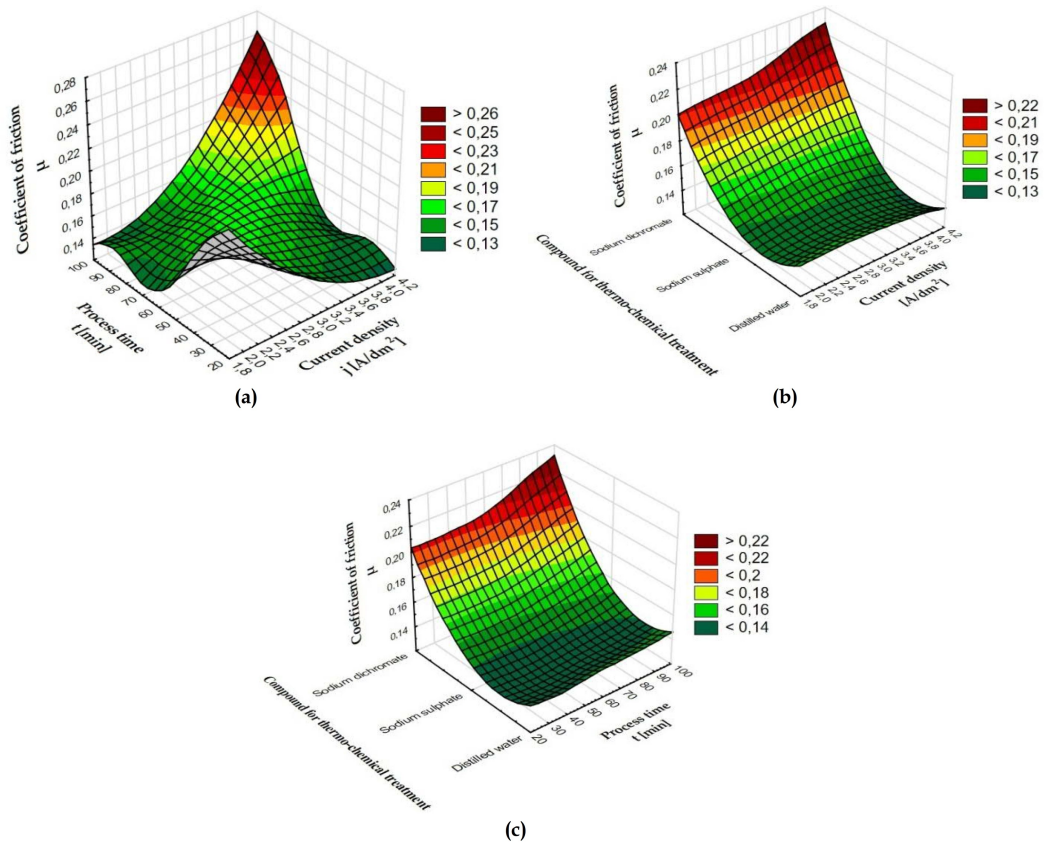


Fig.4. Dependence of coefficient of friction μ on: (a) process time and current density, (b) chemical compounds used to modify layer and current density, (c) chemical compounds used in layer modification and process time

Figure 4 shows the dependence of the coefficient of friction of the contact on the production parameters and compounds used for the thermo-chemical treatment of the layers.

Figure 4a shows a significant increase in the coefficient of friction for the contact of the T7W pin and the layers produced in more than 90 minutes, and a current density above 4 A/dm². You can also see the elevation of the graph background for low anodizing time and current density. A reduction in the coefficient of friction is visible for the contact of the T7W pin and the layers produced within 60 minutes for the extreme values of current density. Charts 4b and 4c show a similar distribution. A reduction increase in the coefficient of friction can be seen with the use of sodium dichromate, which achieves the highest value for the contact of the polymer with the layer produced at the highest current density and process time. The lowest values were observed for sodium sulphate used in the thermo-chemical treatment solution.

Table 8 presents the values of the mass wear of the T7W polymer pin cooperating with the Al₂O₃ layers produced in the anodizing process according to Table 3 (after thermo-chemical treatment).

The lowest values of mass wear were observed for the polymer pin cooperating with the layers treated in the sodium dichromate solution (02C, 02D, 02H). Sodium dichromate lowered the pin mass wear to the lowest value (0.319 mg) for the sample produced at 3 A/dm² for 60

Table 8. Mass wear of T7W pin in contact with layers after thermo-chemical treatment

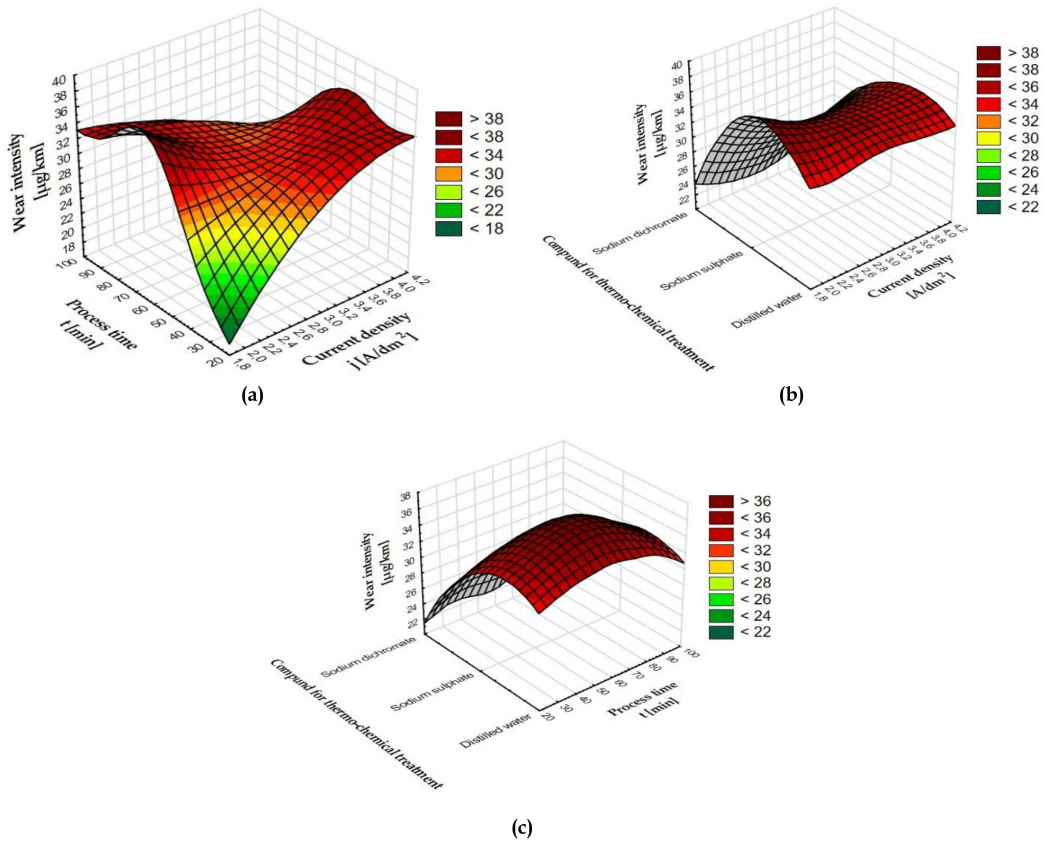
Sample	Mass wear [mg]
02A	0.490
02B	0.497
02C	0.340
02D	0.379
02E	0.559
02F	0.505
02G	0.521
02H	0.319
02I	0.496
02J	0.480
02K	0.535

minutes. The highest value was observed for the contact with sample 02E (0.559 mg) treated in the sodium sulphate solution and produced during anodizing at 2 A/dm² for 60 minutes.

Figure 5 shows the dependence of the T7W pin wear intensity on the production parameters and compounds used for the thermo-chemical treatment of the layers.

Analysing the surface graphs of the dependence of the wear intensity of the T7W pin on the parameters of layer production and their thermo-chemical treatment, a significant reduction in the intensity of wear of the

Fig.5. Dependence of the wear intensity of T7W pin on: (a) process time and current density, (b) chemical compounds used for layer modification and current density, (c) chemical compounds used in layer modification and process time



polymer pin towards the minimum values of the process time and current density can be noticed (Fig. 5a) Figure 5b shows a reduction in the intensity of the wear of the pin towards the use of sodium dichromate in the thermochemical treatment solution, increasing towards sodium sulphate (especially for the extreme current values), decreasing towards distilled water. Figure 5c shows a decrease in the wear intensity of the pin associated with the use of sodium dichromate in solution, increasing towards the use of sodium sulphate, decreasing for extreme process times.

For the sake of comparison, micrographs of the samples after the tribological test, produced in the same anodizing conditions (3 A/dm², 298 K and 60 minutes), differing in the compound for thermo-chemical treatment or its absence, are presented in Figure 6. The micrographs were taken using a metallographic microscope.

Significant differences in the intensity of the application of the sliding film on the Al₂O₃ layer were noticed. The sample without thermo-chemical treatment (01K) is characterized by the most intense trace of the sliding film because it has a high surface porosity, which has a significant impact on wear [21]. Sample 02H is characterized by the least visible sliding film and at the same time the lowest mass wear, because the pores were covered with a sub-layer - a thin layer of film visible.

Summarizing the tribological tests, it can be stated that the use of a sodium dichromate solution in the thermochemical treatment process increases the coefficient of friction with a simultaneous significant decrease in the mass wear of the material, regardless of the conditions of layer production. The intensity of the wear intensity of the pin cooperating with the untreated sample was 36 µg/km. The lowest mass wear was measured for the pin cooperating with the 02H sample and it was 21.33 µg/km. The use of distilled water and sodium sulphate during processing contributed to a slight reduction in the mass wear of the material (comparison of samples 01K, 02G, 02K, 02H).

In order to assess the wear and determine the functional properties of Al₂O₃ layers (without and after thermo-chemical treatment), before and after the tribological test, the surface geometric structure (SGS) was measured. The measurements were also aimed at determining the roughness parameters of the Al₂O₃ layers before and after the tribological test in sliding contact with the T7W material.

For comparative purposes, Figure 7 shows isometric images of the Al₂O₃ layers produced in the anodizing process at the current density of 3 A/dm², with the electrolyte temperature of 298 K for 60 minutes. The differences in the production of the samples resulted from

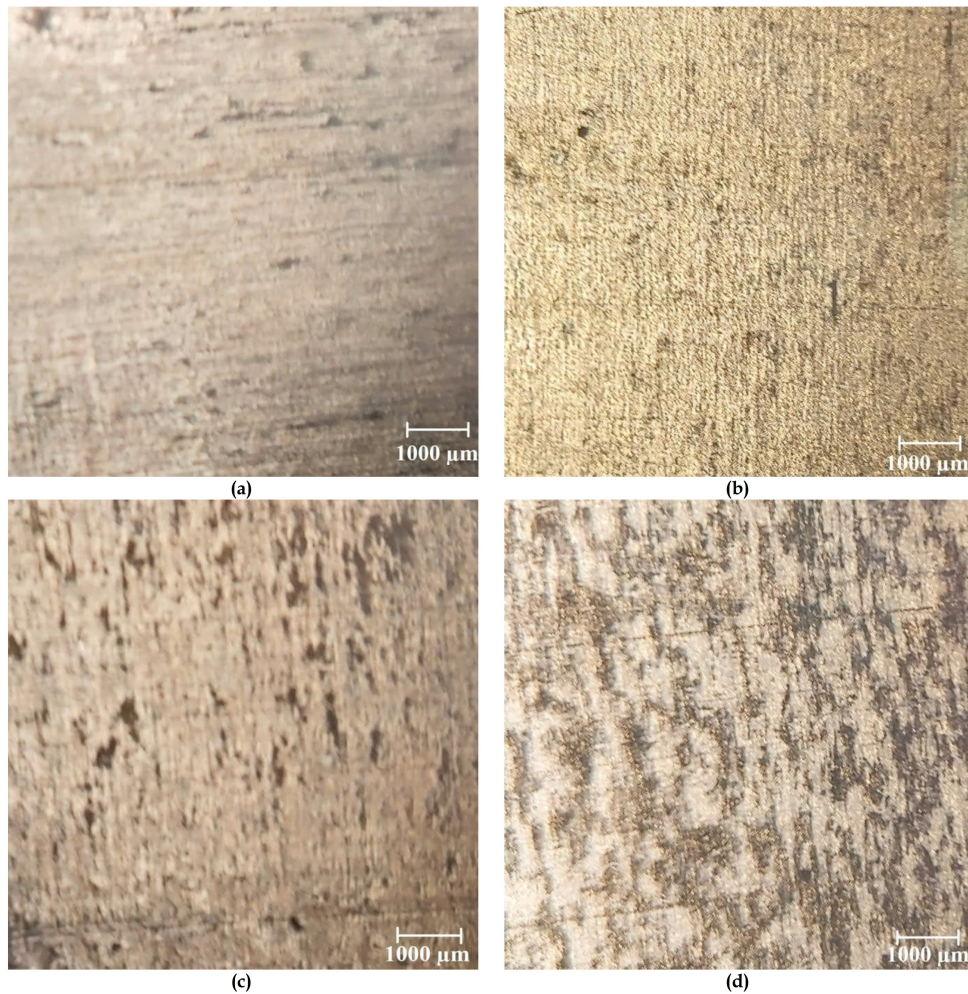


Fig.6. Comparative micrographs of Al₂O₃ layers after tribological test, differing in thermo-chemical treatment: (a) sample 01K, (b) sample 02G, (c) sample 02K, (d) sample 02H

the applied thermo-chemical treatment after anodizing, or the lack of it.

Taking into account the layers before the tribological test, the high roughness of the 02H sample treated in the sodium dichromate solution can be noticed. Most probably, during the thermo-chemical treatment, sodium dichromate deposited on the oxide layer (unevenly) creating a high roughness sub-layer. The use of distilled water and sodium sulphate did not significantly affect the geometric structure of the surface of the layers before treatment.

When analysing the isometric images after the tribological test, several important facts can be taken into account. The tribological test conducted with the layer without thermo-chemical treatment (sample 01K) and after treatment with distilled water (sample 2G) made it smooth over the entire surface. The thermo-chemical treatment carried out in the sodium dichromate solution (sample 02H) contributed to a much smaller reduction of surface roughness due to friction, and the smoothing is not even. This is most likely due to the uneven abrasion of the sodium dichromate sub-layer (of varying thickness) and

the slight application of a sliding film to the surface of the layer. The tribological test performed with the 02K sample treated in the sodium sulphate solution also contributed to a reduction in the surface roughness; nonetheless, depressions and places of uneven application of the sliding film are visible.

Table 9 presents the amplitude parameters (providing the most important information about the SCS change) and the parameter of the load curve (Svk) of selected Al₂O₃ layers before and after the tribological test. The following amplitude parameters are listed: Sa - arithmetic mean deviation of the surface unevenness height from the reference plane, Sq - mean square deviation of the surface unevenness height from the reference plane, Sp - height of the highest surface elevation, Sv - depth of the lowest surface depression, St - vertical distance between the top of the highest peak and the lowest depression of the surface, Sz - surface unevenness height for 10 points (five of the highest peaks and five of the lowest depressions), Ssk - the asymmetry (skewness) coefficient of the surface topography (ordinate) distribution and the parameter of the load curve Svk - reduced depth of surface depressions.

Fig.7. Surface isometric images: (a) sample 01K, (b) sample 02G, (c) sample 02H, (d) sample 02K, 1 - before the tribological test, 2 - after tribological test

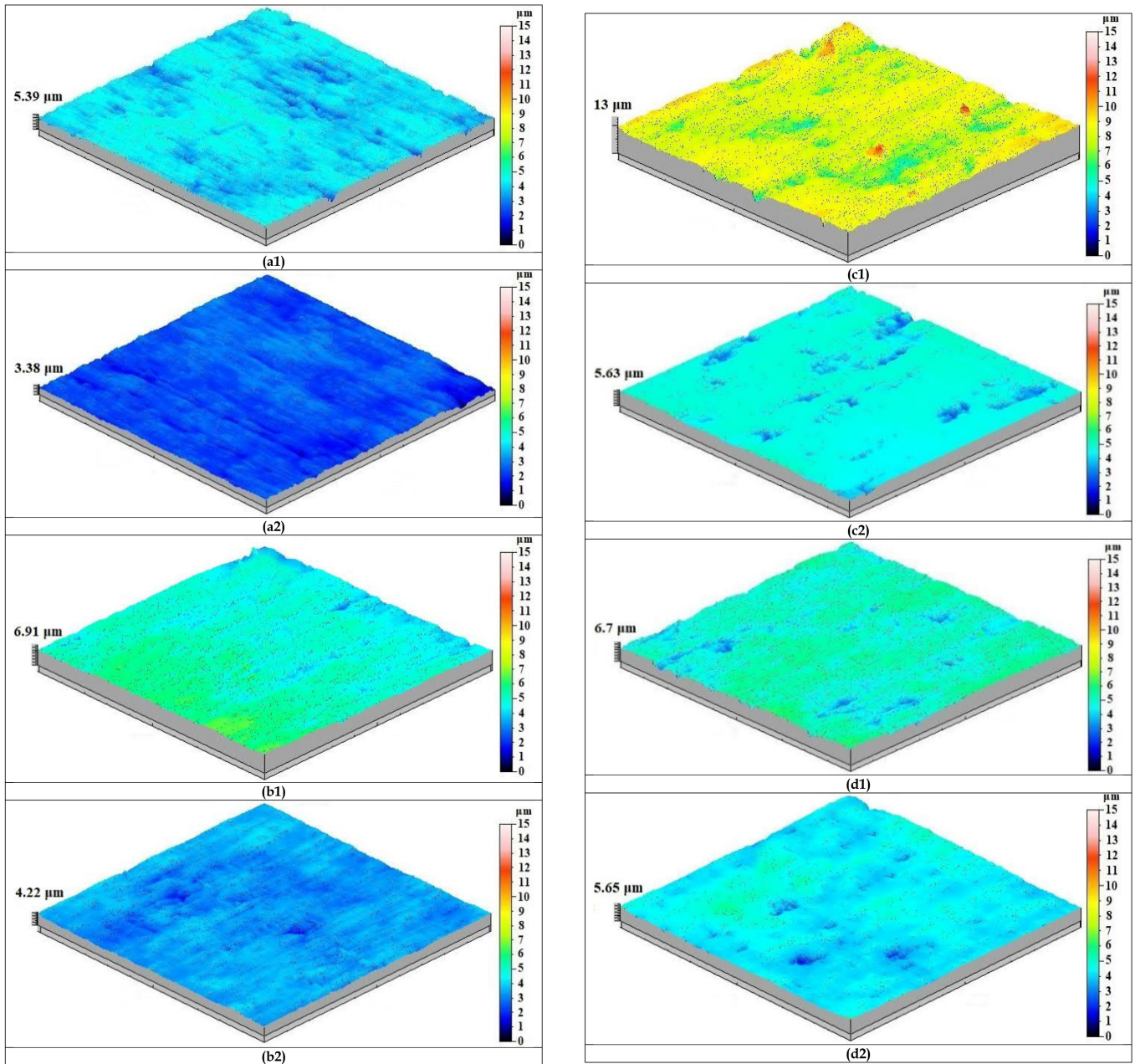


Table 9 presents the amplitude parameters and the parameter of the load curve for comparative purposes for samples with different or no thermo-chemical treatment.

Taking into account the amplitude parameters of the oxide layers, before the tribological test, samples with the same parameters of oxide layer production were compared (current density - 3A/dm², electrolyte temperature 298 K and process time - 60 minutes). The use of sodium dichromate for the thermo-chemical treatment of the Al₂O₃ layer (sample 02H) resulted in a significant increase in surface roughness resulting in a rise in the amplitude parameters (Sa, Sq, Sp, Sv, St and Sz) and Svk parameters. Sodium dichromate also contributed to a reduction in the asymmetry coefficient, i.e. the Ssk parameter, in relation to

the unmodified layer. Sodium sulphate used to modify the 02K sample did not significantly affect the Sa, Sq, Sp, Sv, St, Sz and Svk parameters, and only slightly reduced the Sk and Ssk parameters. The last compound used to modify the layer was distilled water (sample 02G). It contributed to a reduction in the Sa, Sq, Sp, Sv, St, Sz, Ssk and Svk parameters.

When analysing the amplitude parameters and the parameter of the load curve determined after the tribological test for the layers produced employing the same anodizing parameters, a demonstrated reduction in most of the amplitude parameters (Sa, Sq, Sp, Sv, St and Sz) and Svk parameter can be noticed and an increase in the Ssk parameter for samples 01K, 02H (without

Table 9. Amplitude parameters and the parameter of the load curve of selected samples with differences in thermo-chemical treatment

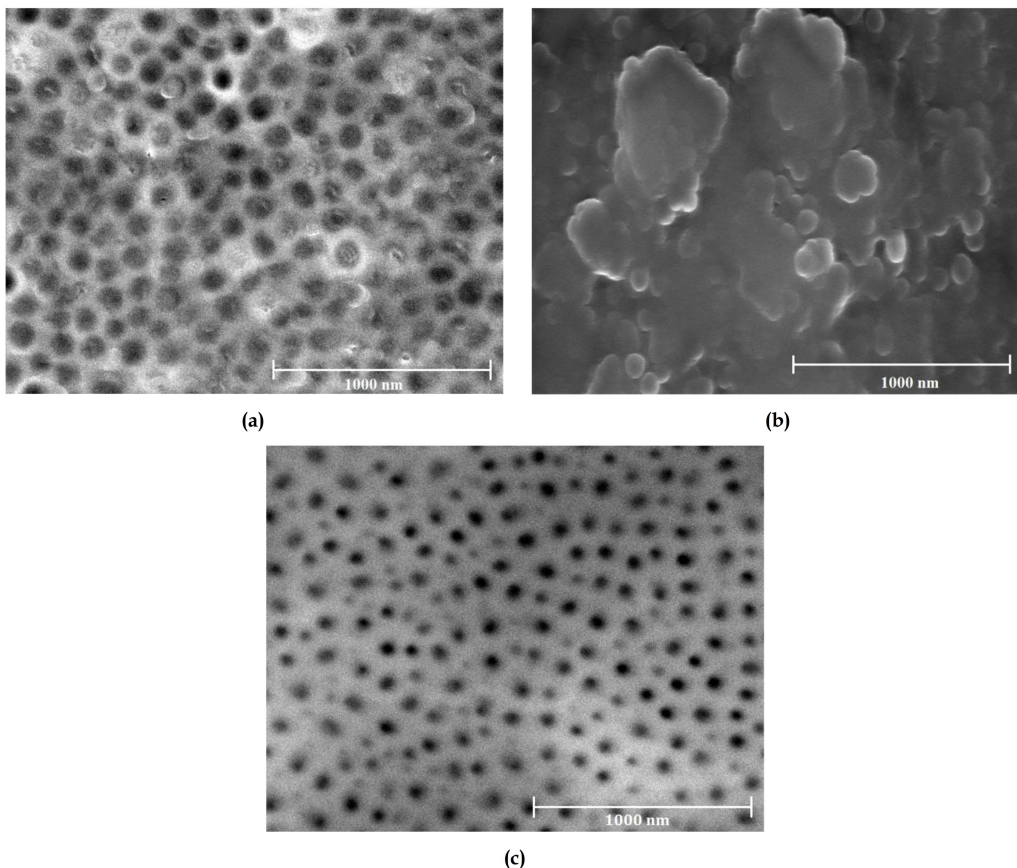
Sample	Compound to be treated	Before/after friction	Sa [μm]	Sq [μm]	Sp [μm]	Sv [μm]	St [μm]	Sz [μm]	Ssk [μm]	Svk [μm]
01K	-	Before	0,408	0.541	2.752	4.464	7.216	5.763	-1.155	0.857
		After	0.261	0.336	1.024	2.352	3.376	2.923	-0.446	0.455
02G	Water	Before	0.241	0.317	0.704	2.72	3.424	2.586	-1.326	0.507
		After	0.242	0.324	0.944	3.296	4.24	3.635	-1.132	0.483
02H	Sodium dichromate	Before	0.69	0.963	7.36	8.176	15.536	11.36	-1.334	1.78
		After	0.252	0.389	6.912	3.392	10.304	5.536	1.561	0.597
02K	Sodium sulphate	Before	0.41	0.551	1.84	4.864	6.704	5.398	-1.318	0.957
		After	0.271	0.413	1.44	4.208	5.648	5.104	-2.057	0.846

modification and with sodium dichromate). The Ssk parameter determined for the 02H sample is positive and the highest among the analysed layers. For sample 02K (modification with sodium sulphate), all the parameters were reduced after the tribological test (Sa, Sq, Sp, Sv, St, Sz, Ssk and Svk). The last analysed surface was sample 02G subjected to thermo-chemical treatment in distilled water. The tribological test caused a slight increase in the amplitude parameters (Sa, Sq, Sp, Sv, St, Sz, Ssk) and a significant reduction of the Svk parameter.

In order to observe the surface of the oxide layers of the samples with the extreme values of coefficient of friction μ and mass wear, micrographs of the surface morphology were taken using a scanning microscope. A magnification of 50,000x was used for the morphology micrographs.

The surface porosity of sample 01D (Fig. 8a) and 01K (Fig. 8c) is visible on the surface morphology micrograph of the sample, characteristic for Al₂O₃ layers. The use of thermo-chemical treatment in sodium dichromate for the 02H sample contributed to complete sealing of the porous

Fig.8. Surface morphology of Al₂O₃ layers: (a, c) without thermo-chemical treatment - sample 01D, 01K (b) after thermo-chemical treatment in sodium dichromate - sample 02H



Al₂O₃ layer and the formation of a sub-layer (no visible porosity of the layer surface) - Figure 8b.

4. Conclusion

The tribological tests showed the influence of the thermo-chemical treatment of layers on both coefficient of friction μ and mass wear. The use of sodium dichromate to modify the layers caused an increase in coefficient of friction μ , while reducing the mass wear of the material during sliding cooperation. Comparing the samples produced under the same conditions, differing only in the compound used for the thermo-chemical treatment, a significant reduction in the wear of the polymer from 36 $\mu\text{g}/\text{km}$ (layer without treatment) to 21.33 $\mu\text{g}/\text{km}$ (thermo-chemical treatment with dichromate sodium) was observed. The use of distilled water and sodium sulphate resulted in only a slight reduction in the wear intensity of the plastic. Stereometric tests performed before and after the tribological test showed that the use of sodium dichromate in the thermo-chemical treatment of Al₂O₃ layers causes a rise in the amplitude parameters (surface roughness). During the tribological test with the Al₂O₃ layer treated in the sodium dichromate solution, a reduction in the high surface roughness (shear elevation) occurs. The surface morphology tests carried out on the layer with the highest mass wear (sample 01D) and on the surface with the lowest mass wear (sample 02H) show that the 01D sample has a porous surface characteristic for oxide layers. On the other hand, the 02H sample, subjected to thermo-chemical treatment in sodium dichromate, is characterized by complete sealing of the porous layer and its covering with a type of sub-layer. The use of sodium dichromate in the thermo-chemical treatment of Al₂O₃ layers increases the amplitude parameters (surface roughness) and the Svk parameter influencing the ability of the material to retain on the surface during sliding cooperation. During the tribological test with the Al₂O₃ layer treated in a sodium dichromate solution there is a reduction of high surface roughness (shear of elevations) and filling the cavities with a sliding film together with the sodium dichromate sub-layer. High surface roughness (heat treatment in sodium-dichromate) results in a high coefficient of friction, while the Svk parameter maintains a self-lubricating layer on the sample surface, reduces mass wear. On the other hand, the Al₂O₃ layers are characterized by high surface porosity, which in turn results in higher wear. In turn, the thermo-chemical treatment in sodium dichromate contributed to the formation of a sub-layer on the Al₂O₃ surface and caused the porosity to be covered (reduced), which is associated with lower wear during sliding cooperation.

In the practical application of thermochemically treated Al₂O₃ layers, when connecting the sliding cooperation (e.g. sealing ring with the actuator cylinder), the wear of the guide ring made of plastic will be significantly reduced.

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