COMPARATIVE STUDY ON THE ENERGY CONDITION OF THE Al_2O_3 OXIDE LAYER ON THE ALUMINUM ALLOY

Mateusz NIEDŹWIEDŹ, Marek BARA, Władysław SKONECZNY

University of Silesia in Katowice, Faculty of Computer Science and Materials Science, Institute of Technology and Mechatronics, Department of Surface Layers Technology, Katowice, Poland, EU,
mateusz.niedzwiedz@us.edu.pl, marek.bara@us.edu.pl, wladyslaw.skoneczny@us.edu.pl

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Abstract

The paper presents investigations of the wettability of Al_2O_3 layers produced by the direct-current method and the reference to its geometrical structure and tribological properties. The layers were made on the aluminum alloy EN AW-5251 using direct-current anodizing at varying production parameters (electrolyte temperature, current density, process time). The aluminum plates before the anodizing process were etched in 5 % potassium hydroxide, then whitened in 10 % nitric acid (V). As the electrolyte, an aqueous solution of 18 % sulfuric acid, phthalic acid and oxalic acid was used. Wettability of the surface was determined by the embedded drop method (measurement of the contact angle). Free surface energy was calculated using the van Oss-Chaunhury-Good method. Measurements of the geometric structure of the surface were made by systematic scanning, determining the basic stereometric parameters from the amplitude group before and after the tribological test. Tribological tests were carried out using a tribological tester T-17 for reciprocating motion on a road with a length of 15 km, under conditions of technically dry friction. A constant slip speed of 0.2 m/s was used, a load of 0.5 MPa was used. The tests were carried out at a constant temperature of 298 K and 60 % relative humidity, T7W polymer was used as the tribo partner. Using the scanning microscope (SEM) images of the surface morphology of Al_2O_3 layers were made at the magnification of 5,000x allowing observation of pores.

Keywords: Direct-current anodizing, surface wettability, surface geometric structure, tribological properties, thin films

1. INTRODUCTION

In today's times of intensive industrial development, and consequently material engineering, there is a growing demand for materials with different mechanical properties [1]. Aluminum has many advantages such as low density or good electrical and thermal conductivity, but it also has significant drawbacks, including high susceptibility to adhesive adhesion in friction nodes [2,3]. In order to eliminate this defect, the aluminum is anodized to form an Al_2O_3 layer. The oxide layer is characterized by a much greater hardness than aluminum alloys and pure aluminum (depending on the anodizing conditions), it also has anti-corrosion and electro-insulating properties. Elements made of aluminum with applied Al_2O_3 layers are widely used in friction nodes. The change of the anodizing parameters (electrolyte temperature, process time, current density) allows to create layers with different mechanical, tribological and energetic properties [4,5]. The energy state of the surface layer has a significant influence on the tribological properties, which is why it is so important to depend the size of the contact angle (free surface energy) on the anodizing conditions and tribological parameters. Changing the energy properties of the surface layer has a significant impact on attracting lubricants in the friction nodes, which has a direct impact on friction and abrasive wear [6].

The paper presents comparative studies of the energy state of the Al_2O_3 layer along with stereometric studies (studies of the geometrical structure of the surface), tribological processes and the morphology of the surface of the layers.

2. RESEARCH METHODOLOGY

2.1. Research material

Al_2O_3 layers were made on metal plates with an area of 0.1 dm^2 made of aluminum alloy EN AW-5251. Plates before anodizing were subjected to pickling in KOH, then bleached in HNO_3. 5 oxide layers were prepared on the aluminum surface, anodizing for each of them took place under different conditions (current density, electrolyte temperature, anodizing time). The ternary electrolyte from sulfuric acid, oxalic acid and phthalic acid was used for anodising. The anodizing conditions for the produced layers are shown in **Table 1**. Samples A and B after the anodizing process were rinsed in distilled water for 1 h.

T7W composite was used as a tribo-partner in sliding association. T7W composite is a material that has been produced on a PTFE matrix with a dispersion phase in the form of technical coal. The material, in cooperation with metals, is characterized by a low coefficient of friction. T7W material is used in pneumatic (guide rings) and hydraulic systems.

Table 1 Anodizing conditions

Sample	Current density j [A/dm^2]	Temperature T [K]	Process time t [min]
A	4	313	20
B	4	293	20
C	2	293	60
D	3	303	60
E	3	293	60

2.2. Research position

Geometric surface structure (SGS) investigations were performed by systematic scanning using a profilograph. The analysis consisted in determination of basic stereometric parameters from the amplitude group, profile together with isometric visualization and load-bearing curves.

Using the scanning microscope (SEM) images of the surface morphology of the Al_2O_3 layers were taken at the magnification of 5,000x. The thickness measurements of the oxide layers were made using the contact method using the Dualscope MP40 thickness gauge.

The SFE calculations were made by measuring the contact angle for two polar liquids (α-bromonaphthalene, diiodomethane) and two nonpolar (glycerin, water). Measurement of the contact angle was done by applying 10 drops of each liquid to the Al_2O_3 layer using a micropipette, then taking a picture through a camera connected to a computer equipped with appropriate software to measure the angle and calculations of SFE.

The average contact drop angle for each sample was used to calculate the SFE using the van Oss-Chauhury-Good method. Tribological tests were carried out on the T-17 tester. The tests were carried out under technically dry friction conditions at a temperature of 298 ± 1 K and atmospheric humidity of 60 ± 10 %. The tests were carried out on a friction road of 15 km, with a constant speed of 0.2 m/s, with a load of 0.5 MPa. The conducted tests allowed to determine the coefficient of friction and linear wear.

3. RESULTS AND DISSCUSION

3.1. Analysis of the geometric surface structure (SGS)

Table 2 shows the amplitude parameters before the test and after the tribological test for all samples. The highest values of amplitude parameters have the sample D, while the lowest sample E. Both samples were anodized for 60 minutes, their thickness is greater than 50 μm.

Table 2 Amplitude parameters before and after the tribological test

	Before the tribological test				After the tribological test			
Sample	**Ra [µm]**	**Rv [µm]**	**Rz [µm]**	**Rp [µm]**	**Ra [µm]**	**Rv [µm]**	**Rz [µm]**	**Rp [µm]**
A	0.512	3.144	4.795	1.652	0.381	1.973	2.773	0.801
B	0.367	1.896	3.162	1.265	0.259	1.538	2.294	0.756
C	0.683	4.293	7.261	2.968	0.292	1.482	2.162	0.681
D	0.694	4.701	8.232	3.532	0.293	1.851	2.587	0.736
E	0.355	2.093	3.041	0.947	0.282	1.819	2.679	0.859

The friction and wear tests caused the smoothing of the surface of the oxide layer, which contributed to the reduction of the amplitude parameters. The reduction of roughness after friction can also be seen in the figure showing the roughness profile () and isometric images together with the load curves (**Figure 2**). From the load curves it can be read that as a result of friction, the supporting part of the tips increased, while the supporting part of the pits decreased.

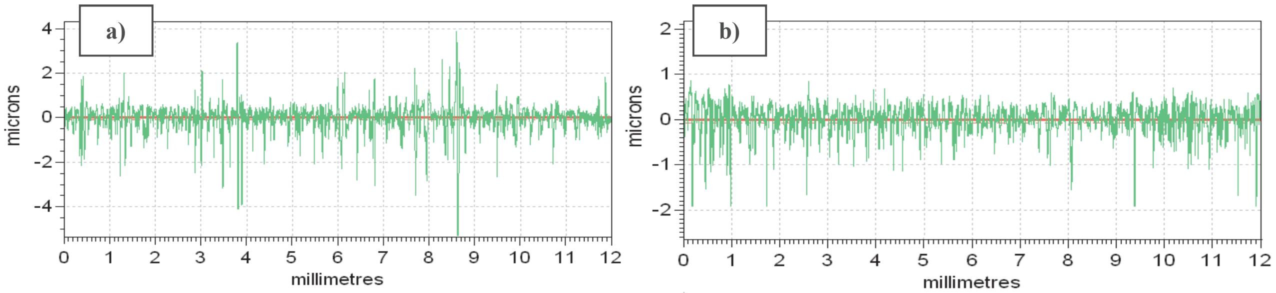

Figure 1 Surface roughness profile of the oxide layer of the sample produced in 3 A/dm^2 at the electrolyte temperature of 303 K: a) before the tribological test, b) after the tribological test

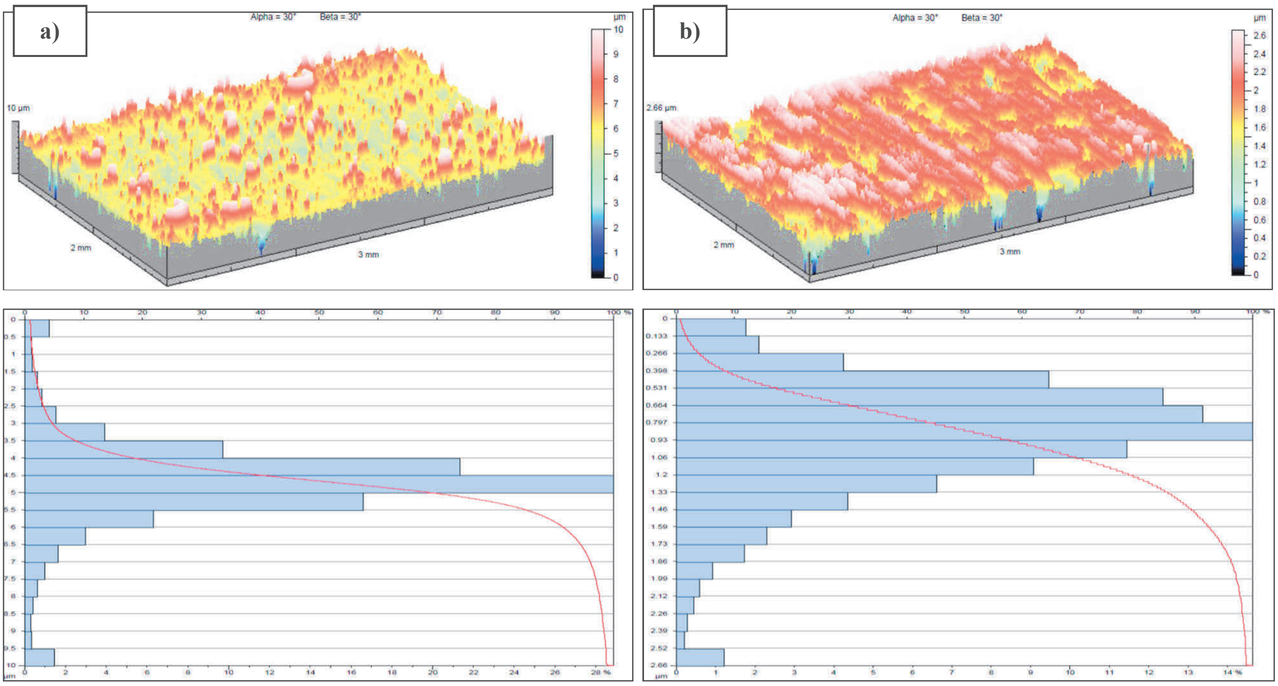

Figure 2 Isometric surface images for a sample produced in 3 A/dm^2 at a temperature of 303 K electrolyte along with Abotta-Firestone curves: a) before the tribological test, b) after the tribological test

3.2. Analysis of layer surface morphology

Images of the surface morphology of Al_2O_3 layers produced on EN AW-5251 aluminum alloys are shown in **Figure 4**. Images were taken at 5000x magnification, which allowed observation of the layer microstructures. In the images, one can notice the micropores characteristic of oxide layers, the size of which varies depending on the anodizing conditions.

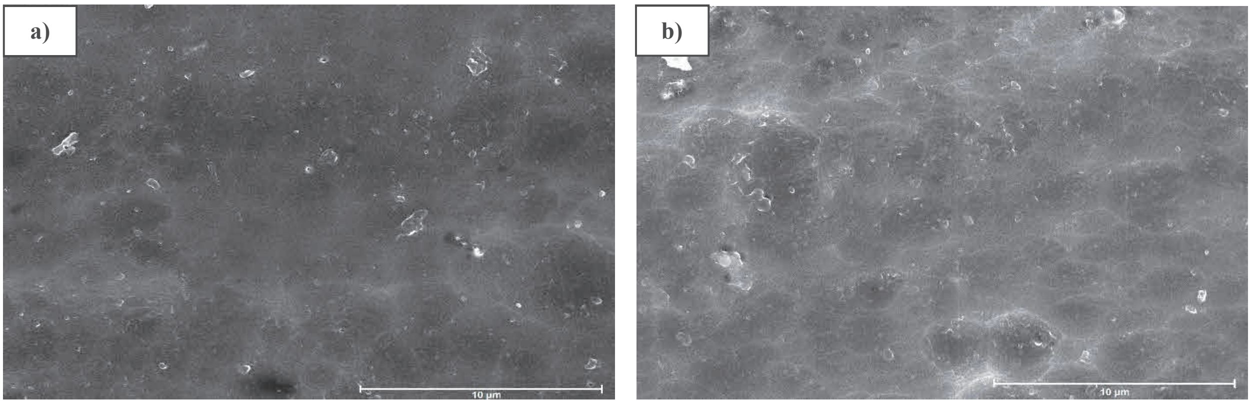

Figure 3 Images of surface morphology of oxide layers produced at current density: a) 4 A/dm^2, b) 2 A/dm^2

3.3. Layer thickness measurement and free surface energy

The results of measurements of oxide layer thickness for individual samples and measurements of the contact angle with the free surface energy calculated using the van Oss-Chauhury-Good method are presented in **Table 3**. It can be concluded that the contact angle for distilled water is inversely proportional to the thickness of the Al_2O_3 layer, so im thicker layer, the lower the contact angle. In turn, SFE is inversely proportional to the contact angle and therefore directly proportional to the thickness of the oxide layer.

Table 3 Thickness, contact angle and free surface energy of Al_2O_3 layers

Sample	Thickness [µm]	Contact angle [°]	SFE [mJ/m^2]
A	23.6	84.3	39.05
B	26.3	83.4	39.3
C	36.62	71.8	40.54
D	50.22	69.55	41.27
E	52.88	61.66	48.44

3.4. Analysis of tribological properties

Figure 4 shows the results of linear consumption measurements for individual samples. It can be noticed that the consumption value changes depending on the layers anodizing conditions. The smallest rope wear was determined for sample A, it is a sample with the smallest thickness of the oxide layer (23.6 µm) and the smallest value of free surface energy (39.05 mJ/m^2). It was anodised at the highest electrolyte temperature of 313 K. The highest linear wear was determined for sample E with the largest thickness (52.88 µm) and the largest free surface energy (48.44 mJ/m^2).

The value of the coefficient of friction is inversely proportional to the wear of the linear oxide layer. The highest value of coefficient of friction was noted for sample A with the smallest thickness and free surface energy, while the smallest value for sample E with the largest thickness and the largest SFE, the value of the coefficient of friction is therefore inversely proportional to the linear wear.

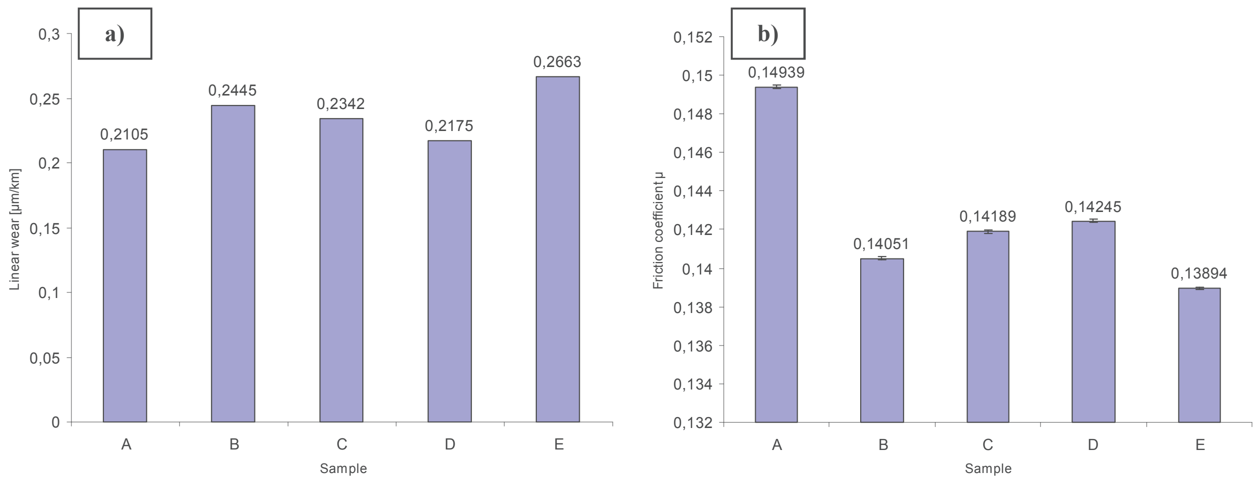

Figure 4 a) linear wear, b) friction coefficient

4. CONCLUSIONS

On the basis of the conducted tests, it can be stated that the change of anodizing parameters (current density, electrolyte temperature, anodizing time) affects the stereometric, energetic and surface morphology properties, which in turn affect the tribological properties of the oxide layers. Samples produced in extreme anodizing parameters were characterized by the smallest and largest layer thicknesses. Sample A produced at a current density of 4 A/dm^2 at the temperature of electrolyte 313 K is characterized by the smallest layer thickness (23.6 µm), it also has the largest contact angle (84.3°), and thus the lowest free surface energy (inversely proportional to the contact angle). It was also noticed that the sample with the smallest layer thickness Al_2O_3 is characterized by the lowest rope wear and the highest coefficient of friction µ. The opposite situation was observed for the sample E produced at the current density of 3 A/dm^2 at the electrolyte temperature of 293 K with the largest layer thickness (52.88 µm), where the contact angle is the smallest (61.66°), SFE the largest. Sample E is characterized by the highest linear wear and the lowest coefficient of friction. It was also noticed that increasing the electrolyte temperature increases the surface roughness of the oxide layer.

The results of the investigation appear to be of great economic interest in wide area of a industry due to the durability of the products and ultimately resulting waste [7-9]. It may be also useful in industry management in the planning phase [10,11], partial surface protection with light heat load [12-14]. Obtained information should be considered especially during difficult image analysis of 3D surface layer structure [15]; ultimately included in knowledge databases of decision support systems [16] and related parametric or non-parametric methods of effects assessment and uncertainty estimation [17].

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