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TYPE OF WEAR OF ALUMINIUM OXIDE LAYERS DEPENDING ON MANUFACTURING PARAMETERS

RODZAJ ZUŻYWANIA WARSTW TLENKOWYCH W ZALEŻNOŚCI OD PARAMETRÓW WYTWARZANIA

Keywords: anodizing, oxide layers, scratch test, aluminium alloys.

Abstract: The article presents the type of wear of Al_2O_3 layers produced on the aluminium alloy EN AW-5251 depending on the production parameters. Oxide layers were produced by using DC anodizing in a ternary electrolyte at variable current density and electrolyte temperature. The layer scratch tests were carried out using a Micron-Gamma microhardness tester. The scratches of oxide layers were tested for the geometric structure of the surface using a Form TalySurf 2 50i contact profilograph. Contact thickness measurements were also made using a Dualscope MP40 device based on the eddy-current method. Using a scanning microscope (SEM), photos of the sample surfaces were taken to show and compare the surface morphology of the anodized layers in various parameters. Based on the research, it can be concluded that changes in the conditions of the production process of Al_2O_3 layers (electrolyte temperature and current density) have an impact on the type of tribological wear and changes in layer thickness. The largest thickness of the oxide layer (19.44 μm) was measured for Sample B produced at a current density of 3A/dm^2 at an electrolyte temperature of 283 K, which was also characterized by the lowest value of the ratio of parameters f1 to f2 (0.584). The smallest thickness (5.32 μm) was measured for the Sample C anodized at 1 A/dm^2 at 303 K, this sample had the largest ratio f1 to f2 (1.068) for the produced Al_2O_3 layers. Thanks to the parameters f1 and f2 and the calculation of their ratio, the wear process for Sample B was determined as scratching and microcutting, while for Sample C as grooving.

Słowa kluczowe: anodowanie, warstwy tlenkowe, test zarysowań, stopy aluminium.

Streszczenie: W artykule przedstawiono rodzaj zużywania warstw Al_2O_3 wytwarzanych na stopie aluminium EN AW-5251 w zależności od parametrów wytwarzania. Warstwy tlenkowe zostały wytworzone poprzez zastosowanie anodowania stałoprądowego w elektrolicie trójskładnikowym przy zmiennej gęstości prądowej oraz temperaturze elektrolitu. Testy zarysowania warstw przeprowadzono za pomocą testera mikrotwardości Micron-Gamma. Zarysowania warstw tlenkowych poddano badaniom struktury geometrycznej powierzchni z użyciem profilografometru kontaktowego TalySurf 2.50i. Wykonane zostały również pomiary grubości warstw tlenkowych metodą stykową z wykorzystaniem urządzenia Dualscope MP40 działającego w oparciu o metodę prądowo-wirową. Z użyciem mikroskopu skaningowego (SEM) wykonane zostały zdjęcia powierzchni próbek w celu pokazania i porównania morfologii powierzchni warstw anodowanych w różnych parametrach. Na podstawie badań można stwierdzić, iż zmiany warunków procesu produkcyjnego warstw Al_2O_3 (temperatura elektrolitu i gęstość prądu) mają wpływ na rodzaj zużycia tribologicznego oraz na zmiany grubości warstwy. Największą grubość warstwy tlenkowej (19.44 μm) zmierzono dla próbki B wytwarzanej przy gęstości prądowej 3A/dm^2 w temperaturze elektrolitu 283 K, która charakteryzowała się również najmniejszą wartością stosunku parametrów f1 do f2 (0.584). Najmniejsza grubość (5.32 μm) zmierzona została dla warstwy próbki C anodowanej w 1 A/dm^2 w temperaturze 303 K, próbka ta cechowała się największym stosunkiem f1 do f2 (1.068) dla wytworzonych warstw Al_2O_3. Dzięki parametrom f1 i f2 oraz przeliczeniu ich stosunku proces zużycia dla próbki B określono jako drapanie i mikroskrawanie, z kolei dla próbki C jako rowkowanie.

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INTRODUCTION

With the current development of technology, the use of aluminium alloys is often insufficient to improve the properties of pure aluminium **[L. 1]**. As a result, the production of Al_2O_3 layers on aluminium alloys by means of anodizing is now the most commonly used surface protection treatment against mechanical damage and corrosion **[L. 2]**. Anodizing creates a thin layer up to several micrometres thick, which significantly improves the mechanical properties of aluminium alloy, which significantly increases the use of aluminium in industrial machine constructions **[L. 3]**. The advantages of aluminium alloys such as high thermal and electrical conductivity, but, above all, low weight, are also preserved **[L. 4]**. There are several popular electrochemical processes for producing oxide layers. Anodizing with alternating current **[L. 5]**, direct current **[L. 6]**, direct voltage **[L. 7]**, alternating current superimposed on direct current **[L. 8]**, and the impulse method **[L. 9]** can be distinguished. Al_2O_3 layers also show low abrasion and are characterized by high microhardness, thanks to which they are widely used in friction pairs **[L. 10]**. By changing the anodizing parameters (current density, electrolyte temperature, process time), one can control both the mechanical and tribological properties of the oxide layers. Scratch tests are performed to determine the mechanical properties and the type of wear of the Al_2O_3 layers **[L. 11]**. The literature lacks detailed studies determining the effect of anodizing conditions of Al_2O_3 layers in the ternary electrolyte on their type of wear, which makes my research characterized by innovation. The purpose of the research was to determine the impact of oxide layer production parameters on their thickness and wear. This article presents the impact of anodizing parameters (current density, electrolyte temperature) on the value of material swelling with a cross-sectional area f1 and the material groove with a cross-sectional area f2, and thus on the type of oxide wear of the layer. Oxide layer thickness measurements, SEM morphological images, and EDS analysis were also performed for selected samples.

MATERIALS AND METHODS

Research material

Al_2O_3 layers produced on the aluminium alloy EN AW-5251 were used as the research material. The alloy used is characterized by high plasticity and very good corrosion resistance. Oxide layers were produced using the method of hard DC anodizing. The surface of the samples used for anodizing was 0.05 dm^2.

Before proceeding with anodizing, each sample underwent a substrate preparation process by chemical treatment. A 5% KOH solution was used for digestion for 20 minutes, and then the samples were bleached for 5 minutes by applying a 10% HNO_3 solution. The temperature of the solutions used was 296 K. At the end of each process, the samples were rinsed in distilled water. Anodizing was carried out in a ternary electrolyte consisting of 18% aqueous sulphuric acid (33 mL/L), oxalic acid (30 g/L), and phthalic acid (76 g/L). DC anodizing was applied using a GPR-25H30D power supply. Mixing of the electrolyte during the anodizing process at 100 rpm was done mechanically and the direction of rotation was changed after 10 minutes. A constant anodizing time of 20 minutes was used for all samples.

In order to determine the input parameters of anodizing, a full experiment plan with two variables (current density, electrolyte temperature) was used. The anodizing time for all layers was 20 minutes. **Table 1** presents a list of factors on a natural and standard scale for anodizing Al_2O_3 layers.

Table 1. List of factors on a natural and standard scale for Al_2O_3 layers produced in the anodizing process
Tabela 1. Zestawienie czynników w skali naturalnej oraz unormowanej dla warstw Al_2O_3 wytworzonych w procesie anodowania

Sample	Controlled factors			
	On a natural scale		On a standard scale	
	Current Density j [A/dm^2]	Electrolyte Temperature T [K]	x1	x2
A	1	283	-1	-1
B	3	283	1	-1
C	1	303	-1	1
D	3	303	1	1
E	1	293	-1	0
F	3	293	1	0
G	2	283	0	-1
H	2	303	0	1
I	2	293	0	0

Research methodology

Measurements of Al_2O_3 layer thickness were made by contact method using a Fischer Daulscope MP40 instrument, which uses the eddy current method for measurements. Ten measurements over the entire length of the sample, which were then repeated three times, made up the average layer thickness of the individual sample. Layer scratch tests were carried out using a Micron-Gamma device. The load used during the test was 4 ± 0.01 N. A Rockwell diamond indenter with a tip radius of 0.2 mm was used. The Al_2O_3 scratches were subjected to the surface geometric structure (SGS) analysis using a Form TalySurf Series 2.50i profilometer. In order to determine the parameters of tribological wear, a method of systematic scanning on a transverse profile was used. Images of transverse profiles were made using TalyMap Universal software.

Surface morphology tests of Al_2O_3 layers were performed using a Hitachi S-4700 scanning microscope. A 50,000x magnification was used to observe the surface of the layers. Chemical analysis of the Al_2O_3 layer was performed using a Noran Vantage EDS analyser attached to a scanning microscope.

RESULTS AND DISCUSSION

Averaged values of Al_2O_3 layer thickness measurements are presented in **Tab. 2**. Significant differences in the thickness of individual layers resulting from anodizing conditions have been shown.

Table 2. Summary of average thickness measurements of Al_2O_3 layers

Tabela 2. Zestawienie średnich pomiarów grubości warstw Al_2O_3

Sample	Oxide Layers Thickness d [μm]	Deviation [μm]
A	6.50	0.6
B	19.44	0.6
C	5.32	0.7
D	16.58	0.3
E	5.60	0.4
F	17.92	0.7
G	12.84	1.1
H	10.78	0.5
I	11.10	0.1

The highest thickness of the Al_2O_3 layer (19.44 μm) was measured for Sample B produced at a current density of 3 A/dm^2 at an electrolyte temperature of 283 K. The lowest value of the thickness of the oxide layer (5.32 μm) was measured for Sample C, for which the current density of 1 A/dm^2 was used at an electrolyte temperature of 303 K. It can be stated that the highest current density and the lowest electrolyte temperature contribute to the formation of the thickest layers, while the lowest current density and the highest electrolyte temperature create the thinnest Al_2O_3 layers. A surface plot was made to visualize the effect of current density and electrolyte temperature on the thickness of the oxide layer accurately (**Fig. 1**).

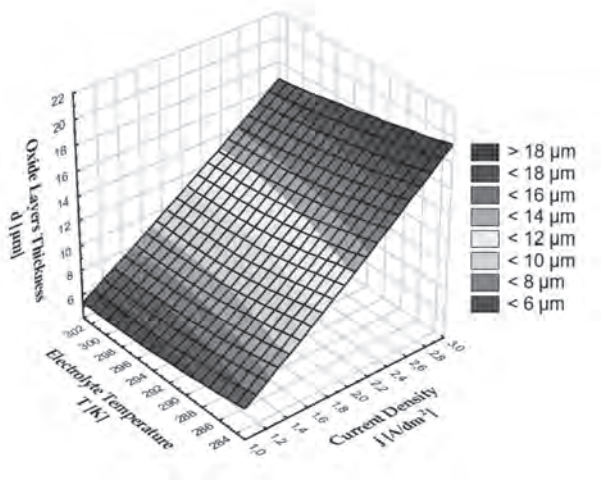

Fig. 1. Dependence of Al_2O_3 layer thickness on electrolyte temperature and current density

Rys. 1. Zależność grubości warstw Al_2O_3 od temperatury elektrolitu i gęstości prądowej

When analysing the impact of anodizing parameters (current density, electrolyte temperature) on the thickness of the oxide layer, it can be seen that the increase in current density during anodizing causes an increase in the thickness of the Al_2O_3 layer. This is due to the increase in electric charge and the transformation of aluminium through electricity into oxide. The increase in electrolyte temperature is associated with a slight decrease in layer thickness, which can be explained by the secondary dissolution of alumina associated with the release of Joule's heat.

Figure 2 shows the cross profiles of the surface of the Al_2O_3 layer and the aluminium alloy EN AW-5251 after the scratch test. The data on the geometric structure of the surface was collected using a profilograph. The images were made using TalyMap Universal software. The area above the zero point (swelling of the material) has been marked with green, the scratch area in red (after the scratch was made).

Images of transverse profiles of Al_2O_3 layers show changes in the shape and surface of areas both below and above the zero point. The mildest rounded surface profiles were noticed for the aluminium alloy without the applied oxide layer. The increase in current density during the production of the Al_2O_3 layer affects the sharpening of surface transverse profiles, which is caused by an increase in the thickness of the oxide layer.

Table 3 shows the values of the ratio of parameter f1 (swelling of the material) to f2 (scratches), along with the type of surface wear of the Al_2O_3 layers and the aluminium alloy determined on the basis of these parameters.

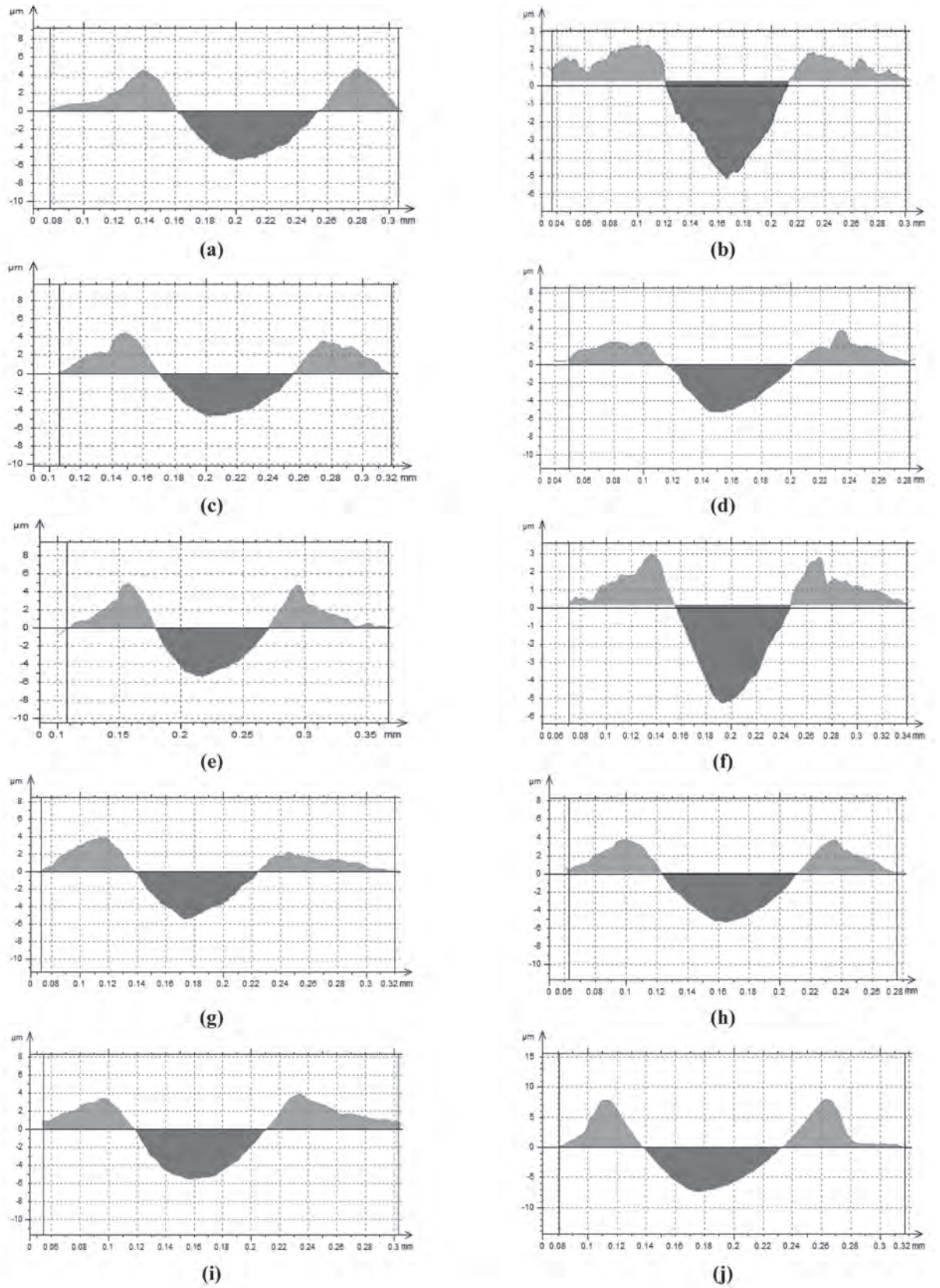

Fig. 2. Transverse profiles of oxide layer and aluminium alloy surface after the scratch test: (a – i): designations according to Table 1; j): aluminium alloy EN AW-5251

Rys. 2. Profile poprzeczne warstwy tlenkowej i powierzchni stopu aluminium po teście zarysowań: (a – i): oznaczenia według tabeli 1; j): stop aluminium EN AW-5251

Table 3. The values of the ratio of f1 (material swelling) to f2 (scratches) and the type of surface wear
Tabela 3. Wartości stosunku parametru f1 (spęcznienia materiału) do f2 (zagłębienia rysy) oraz rodzaj zużycia powierzchni

Sample	f1/f2	Deviation	Wear Process
Aluminium alloy	1.110	0.116	grooving
A	0.926	0.091	scratching, microcutting
B	0.584	0.069	scratching, microcutting
C	1.068	0.087	grooving
D	0.724	0.101	scratching, microcutting
E	0.998	0.104	scratching, microcutting
F	0.697	0.076	scratching, microcutting
G	0.744	0.064	scratching, microcutting
H	0.796	0.067	scratching, microcutting
I	0.787	0.086	scratching, microcutting

Due to the analysis of parameters f1 and f2, the influence of the oxide layer production parameters on their type of wear was determined. It was found that the increase in the Al_2O_3 layer, starting from the aluminium alloy without the oxide layer produced, reduces the ratio of f1 to f2. For aluminium alloy and Sample C (smallest oxide layer thickness), there is a plastic deformation of the surface layer called grooving. The wear process called grooving occurs if f1/f2> 1. The remaining samples tested have a $0<f1/f2\leq1$ ratio, which indicates scratching and microcutting during the wear process.

Figure 3 shows selected images of surface morphology of Al_2O_3 layers taken with a scanning electron microscope (SEM). A magnification of 50,000x was used to observe the nanopores.

Significant changes were observed in the surface morphology of the Al_2O_3 layers resulting from the applied anodizing process conditions. The increase in current density at constant process time and electrolyte temperature causes a significant increase in pore diameter (E and I). The increase in pore size along with the increase in current density is caused by an increase in process speed and a faster increase in oxide layer thickness. Electrolyte temperature also has a significant effect on surface morphology. Comparing Samples A, C, E, an increase in the number of nanopores was observed

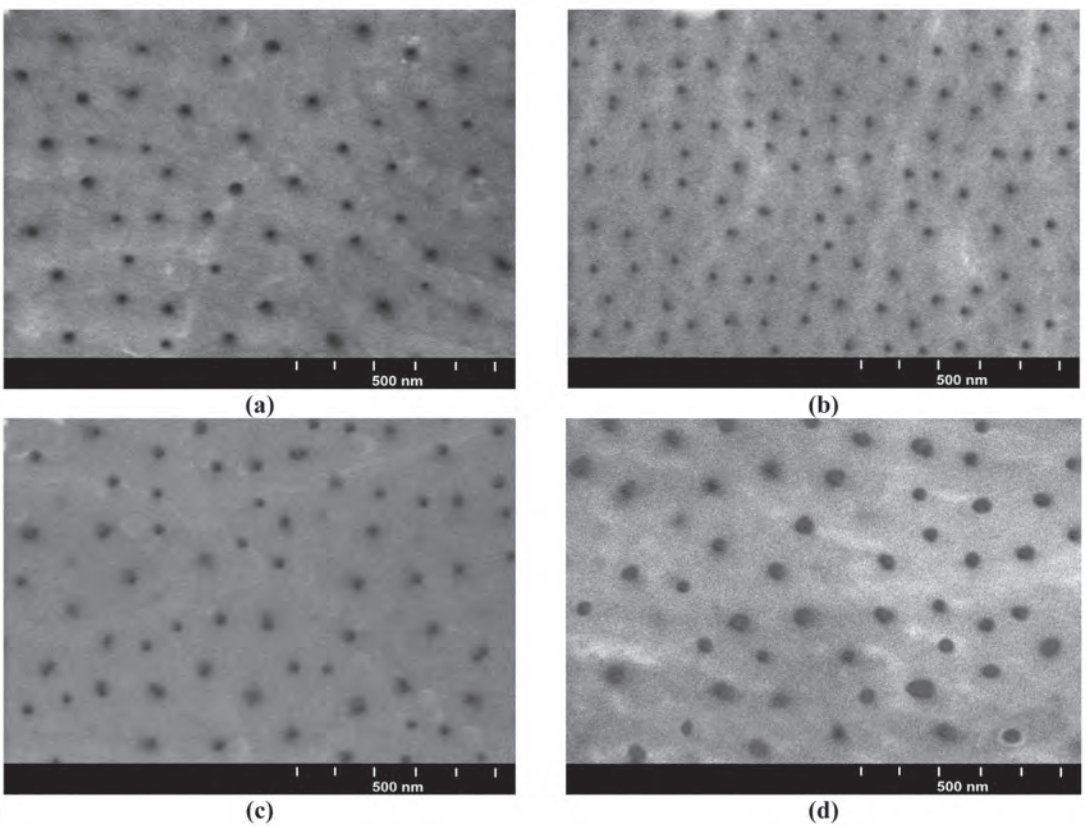

Fig. 3. Images of surface morphology of oxide layer: (a) Sample A, (b) Sample C, (c) Sample E, (d) Sample I
Rys. 3. Obrazy morfologii powierzchni warstwy tlenkowej: (a) próbka A, (b) próbka C, (c) próbka E, (d) próbka I

along with an increase in the electrolyte temperature and a simultaneous decrease in their size, and thus an increase in the thickness of the Al_2O_3 layer.

Table 4 shows the chemical composition analysis (atomic content) of the oxide layer formed in the ternary electrolyte on aluminium alloy EN AW-5251 for an example sample made using an EDS analyser. Figure 4 depicts the EDS spectrum of the oxide layer. The spectrum shows traces of carbon on the surface, which is due to the sputtering of the layers before SEM testing.

Table 4. Chemical composition (atomic content) of the Al_2O_3 layer

Tabela 4. Skład chemiczny (zawartość atomowa) warstwy Al_2O_3

Atomic Aluminium Content [%]	Error of Aluminium Content [%]	Atomic Oxygen Content [%]	Error of Oxygen Content [%]
56.71	±0.23	42.99	±0.51

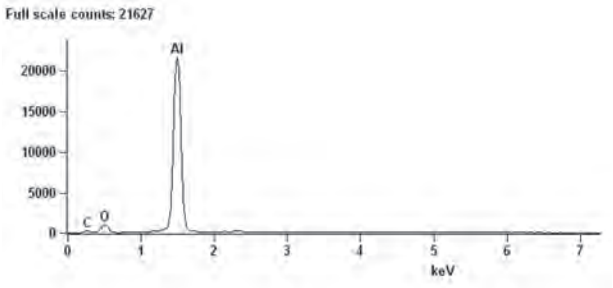

Fig. 4. Graph of EDS spectrum of the Al_2O_3 layer

Rys. 4. Wykres widma EDS warstwy Al_2O_3

The analysis of the chemical composition of Al_2O_3 layers for the sample is similar to stoichiometric calculations of 52.92% aluminium and 47.08% oxygen atomic content. Slight differences may be due to the thickness of the oxide layer.

CONCLUSIONS

After the tests, a significant impact of anodizing parameters on the type of oxide layer wear can be found. The increase in the thickness of the oxide layer occurs with the increase in current density and decrease in electrolyte temperature during anodizing. The thickness of the Al_2O_3 layer has a significant impact on the type of wear. The highest values of the f1/f2 ratio were observed for the smallest layer (Sample C), while the lowest for Sample B with the thickest oxide layer. An increase in the f1/f2 ratio was observed with a decrease in the thickness of the oxide layer. Only for two samples on which tests were carried out as a type of wear was grooving, it is the aluminium alloy surface and the Al_2O_3 layer of the smallest thickness (C). Scratching and microcutting occur for all other samples. An increase in current density with a simultaneous decrease in electrolyte temperature causes an increase in the thickness of the oxide layer, resulting in a change in the type of layer wear from drawing and microcutting to grooving. The change of anodizing parameters also has a significant impact on the shape of the surface transverse profiles, which, with the decrease of the ratio f1/f2, become more and more sharp. The conditions of the oxide layer manufacturing process also have a significant impact on surface morphology, and more specifically the number and size of nanopores.

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