

## PROPERTIES OF COMPOSITE ALUMINIUM OXIDE–GRAPHITE LAYERS OBTAINED BY AN ELECTROLYTIC METHOD

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### Summary

The paper presents the mechanical properties of composite aluminium oxide-graphite surface layers. The layers were obtained by an electrolytic method, on a EN AW-5251 aluminium alloy substrate, in electrolytes with different graphite concentrations. The layers produced were subjected to tests with use of scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The results of tests concerning the microstructure, thickness and microhardness of the layers are presented.

Keywords: composite layer, aluminium oxide, graphite, SEM, XPS

### Właściwości kompozytowych warstw tlenek aluminium-grafit otrzymywanych metodą elektrolityczną

#### Streszczenie

W pracy przedstawiono właściwości mechaniczne kompozytowych warstw powierzchniowych tlenek aluminium-grafit. Warstwy otrzymano metodą elektrolityczną na podłożu stopu aluminium EN AW-5251, w elektrolitach o różnym stężeniu grafitu. Wytworzone warstwy poddano badaniom przy zastosowaniu elektronowej mikroskopii skaningowej (SEM) oraz spektrometrii fotoelektronów (XPS). Przedstawiono wyniki badań mikrostruktury i morfologii powierzchni oraz grubości i mikrotwardości warstw.

Słowa kluczowe: warstwa kompozytowa, tlenek aluminium, grafit, SEM, XPS

## 1. Introduction

More and more attention is paid in the national and international specialist literature to research on the modification of layers directly responsible for durability and reliability of machines. The latest trends in the technology of producing surface layers concern composite layers, whose structure allows a smooth change of properties from the surface to the base material, with the production costs being as low as possible. The oxide ceramic layers,  $Al_2O_3$ , produced via hard anodizing, belong to a group of materials with a strongly

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developed surface. They have good mechanical and tribological properties, which justifies their application in the production of sliding couples [1-4]. Tribological properties can be improved through increasing the resistance to pressure (increasing the hardness) and decreasing the shear strength. Such effect could be achieved by incorporating graphite or molybdenum disulfide into the aluminium oxide layer [5-7]. Tribological tests of pin-on-disc couples, conducted on aluminium oxide – graphite layers produced by the plasma anodizing method, exhibited a four times lower friction coefficient than during tests of layers covered with aluminium oxide only [8]. The tests were carried out in dry friction conditions and they show the influence of carbon content in the oxide layer on the value of resistance to motion.

The authors have attempted to incorporate graphite into the aluminium oxide layer during electrolysis in ambient temperature. This thesis is a continuation of the research on the properties of oxide aluminium – graphite composite layers obtained in electrolytes with a various graphite content and it is complementary to the X-ray analysis of those layers published in Materials Science – Poland [9].

## 2. Research object and methodology

The research object consisted of composite surface layers of aluminium oxide-graphite of a 5 cm<sup>2</sup> area, produced on a substrate of EN AN-5251 alloy. The layers were produced in the process of electrolytic oxidation by direct current method, in a multicomponent electrolyte with an addition of organic acids and graphite of 99% purity. Four electrolytes were used, differing with the graphite content. To the base electrolyte, being an aqueous solution of acids: sulphuric, oxalic and phthalic (sample A), 10 g of graphite per one litre of electrolyte was added, which allowed obtaining the following samples: B – 10 g/l, C – 20 g/l and D – 30 g/l, respectively. The oxidation was conducted with a constant charge of 180 Amin. Current density amounted to 3 A/dm<sup>2</sup> with oxidation time of 60 minutes. The bath temperature was 303 K. The process of composite layers production was preceded by cleaning the aluminium alloy surface through etching in a 5% KOH solution for 40 minutes and in a 10% HNO<sub>3</sub> solution for 10 minutes, followed by rinsing in distilled water in order to remove the electrolyte from the oxide layer.

Examination of the microstructure and morphology was conducted using a Philips XL30 scanning electron microscope with a magnification of 2500 ÷ 200000 x. Transverse microsections were made through grinding and two-stage mechanical polishing, as well as ion etching and polishing with PECS 682 device of Gatan. The conditions of polishing and etching of all layers were: V = 6 keV, I = 300 µA, t = 20 min for polishing and t = 10 min for etching. Since amorphous aluminium oxide does not allow carrying away electrons

knocked off during the reaction of a microscope beam, the tested layers were sputtered with gold and palladium. The sputtering operation was performed also with the PECS 682 device of Gatan company. For the current conditions of  $V = 10$  keV and  $I = 400$   $\mu\text{A}$ , the spraying rate was 3  $\text{\AA}/\text{s}$ . Sputtering was conducted until the Ag-Pd layer's thickness achieved 0.5  $\text{k}\text{\AA}$ .

Identification of the chemical elements and a quantitative analysis of the chemical composition were made with a PHI 5700/660 spectrometer, applying the X-ray photoelectron spectroscopy technique (photoelectrons induced by X-ray radiation). For etching of the indented profile,  $\text{Ar}^+$  ions with energy of 4 keV were used. Sputtering cycles of the indented profile lasted 10 minutes each and were followed by measurements of the chemical composition.

The thickness of the composite layers was measured with a Dualscope thickness gauge, making 20 measurements on the length of the samples.

Microhardness was determined from cross-sections of the layers impressed with Hanemann's microhardness tester under load of 0.3N.

### 3. Research results

The oxide layer structure is one of the main factors determining the properties of the layer. It depends, to a large degree, on the type, concentration, and temperature of electrolyte, as well as oxidation conditions (electric charge density).

Tests of the layers' cross-sections, conducted at magnification of 50,000  $\times$ , show a columnar-fibrous structure, oriented along the direction of its growth as a result of the electric field influence. The pictures taken at the layers' substrate (Fig. 1) show the transformation of a thin barrier layer of a dendritic structure into a proper oxide layer of a columnar structure. In pictures 1b, 1c and 1d, over the barrier layer between the oxide fibres, "bowls" of a spherical structure are visible, whose diameters correspond to the diameters of the graphite used in the tests. The spherical shape of the "bowl" is probably connected with the introduction of graphite into the microstructure of the layers, followed by removal of graphite grains during mechanical treatment of the material. The amount and concentration of the "bowls" depends proportionally on the graphite content in the electrolyte.

Microscopic pictures of surface morphology of an aluminium oxide layer (Fig. 2a) and composite layers of aluminium oxide/graphite (Fig. 2b, 2c, 2d) have exhibited a characteristic porosity of the surface, being the effect of the contact of fibres. The porosity of oxide layers is one of the main factors determining the layer's properties and it conditions the purpose of the layer. It appears from the observation of the above pictures that there are no distinct differences in size and distribution of pores in the layers produced in electrolytes with various graphite concentrations. A computer analysis of binary images of

the coatings has shown porosity in the range of 10-15%. Oxide layers of such porosity are suitable for tribological interaction under dry friction conditions.

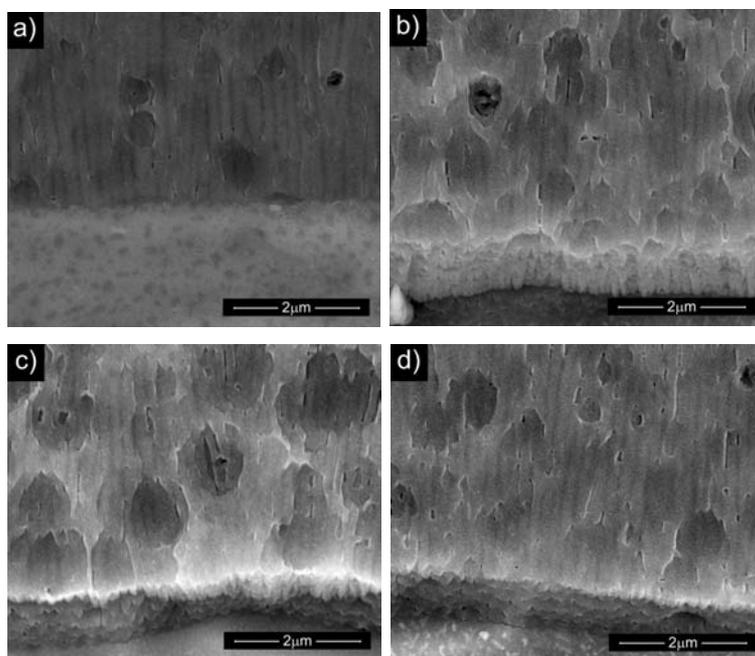


Fig. 1. Microstructure of cross-sections of layers obtained in electrolytes with various graphite concentrations: a) without graphite, b) 10 g/l, c) 20 g/l, d) 30 g/l

XPS detection of the chemical composition of the surface of a composite layer produced in electrolyte containing 20 g of graphite per one litre of electrolyte, performed before sputtering, revealed the presence of 23.01% of carbon, 0.45% of nitrogen, 53.46 of oxide and 23.08 of aluminium.

A detailed analysis of the layer spectra after first sputtering cycles (Fig. 3) has shown the presence of carbon in 3 chemical states. The main line of spectrum C1s occurred at the energy of 285.2 eV, which corresponds to single C-H carbon bondings and is connected with adsorption of organic acids from the electrolyte. At the energy of 289.2 eV, a double bonding of carbon with oxygen, C=O, occurs for this line, as well. It is the effect of contamination with atmospheric coal. After 30 minutes of sputtering, a line of bond energy of 284.6 eV emerges. This bond energy may be ascribed to C-C compounds and associated with the incorporation of graphite into the aluminium oxide layer.

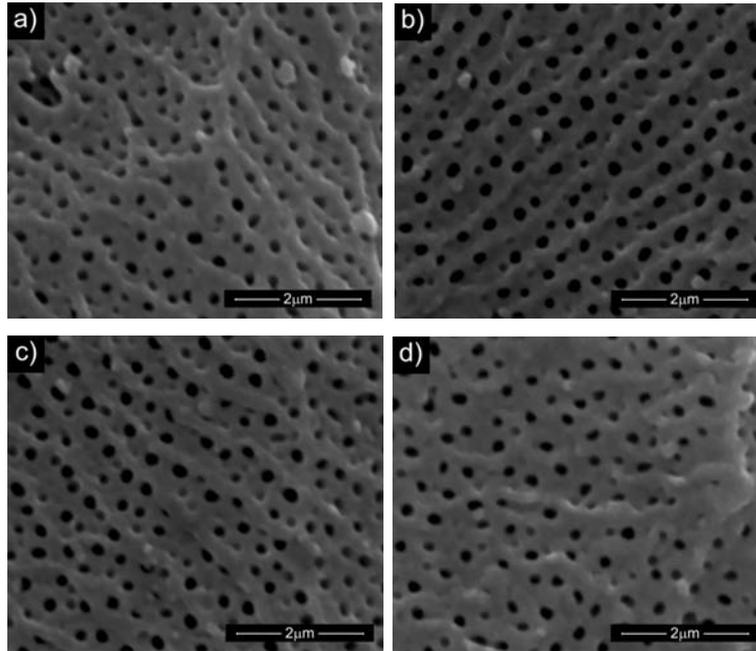


Fig. 2. Surface morphology of layers obtained in electrolytes with various graphite concentrations: a) without graphite, b) 10 g/l, c) 20 g/l, d) 30 g/l

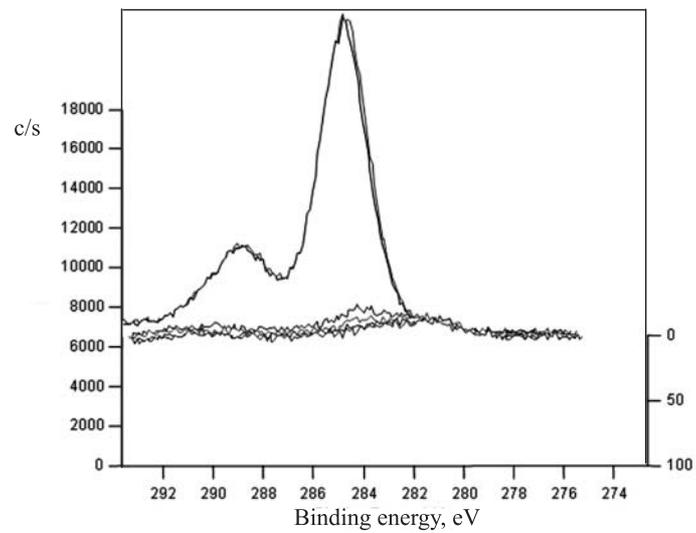


Fig. 3. Detailed analysis of spectra after first sputtering cycles of a layer produced in electrolyte containing 20 g of graphite per 1 litre of electrolyte

A detailed analysis of spectra in last sputtering cycles (Fig. 4) has also shown a bond energy line which can be ascribed to C-C compounds and a line of bond energy of 282 eV. This bond energy can be attributed to compounds of carbon with metals present in the layer substrate.

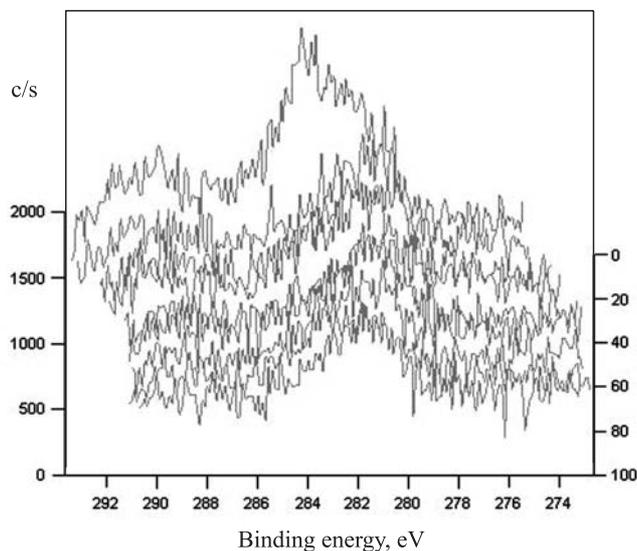


Fig. 4. Detailed analysis of spectra in the last sputtering cycles of a layer produced in electrolyte containing 20 g of graphite per 1 litre of electrolyte

Thickness measurements of all layers have not shown any significant differences (Fig. 5). For both, the oxide layer and composite layers, the average thickness was  $47.3 \pm 0.8 \mu\text{m}$ . The obtained results show that the graphite content in the electrolyte has no influence on the thickness of composite layers.

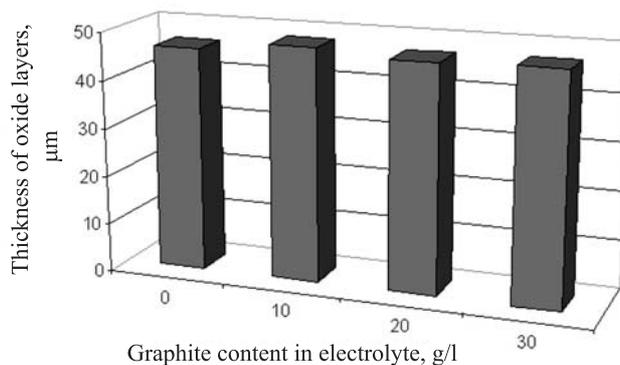


Fig. 5. Influence of graphite content in electrolyte on the layer thickness

The measurement results of six series of indentations made in three zones on the layers' cross-sections have shown a linear change of microhardness from the substrate towards the layer surface (Fig. 6).

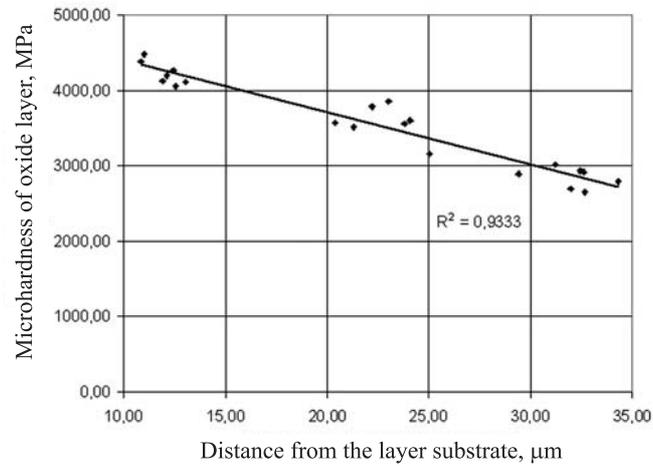


Fig. 6. Influence of the distance from the Al substrate on the layer microhardness

The highest microhardness was recorded in the zone at the substrate of the layer, whereas the lowest one, at the surface. This dependency was visible in all tested layers. When comparing the microhardness of layers produced in electrolytes with various graphite contents (Fig. 7) it was noted that the microhardness increases together with an increasing graphite content in the electrolyte.

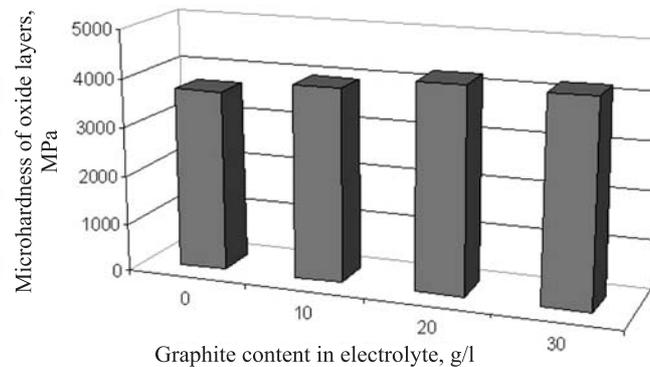


Fig. 7. Effect of graphite content in electrolyte on the layer microhardness

For the measurements performed at a constant distance of 20  $\mu\text{m}$  from the layer substrate, the microhardness of layers amounted, respectively for the samples: A – 3706 MPa, B – 3976 MPa, C – 4242 MPa, and D – 4240 MPa. An increase of the graphite content in the electrolyte to above 20 g/l did not cause any increase of the layer microhardness.

#### 4. Conclusions

Based on the conducted research and analysis of its results, it can be concluded that: the introduction of graphite to the electrolyte composition allows obtaining composite surface layers consisting of aluminium oxide and graphite. Changes in the microstructure of the tested layers depend proportionally on the increasing graphite concentration in the electrolyte, resulting in an increase of microhardness by 13.2%, with keeping similar thickness of the layers. Tests of the chemical composition have corroborated the possibility of incorporating graphite into the entire cross-section of composite layers, which predisposes the layers of aluminium oxide/graphite to a tribological interaction.

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Received in May 2008