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Aluminium oxide composite layers obtained by the electrochemical method in the presence of graphite

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The paper presents a new method of obtaining aluminium oxide composite layers formed by means of hard anodizing in an electrolyte composed of water solution of acids and graphite. The produced layers were subject to tests and their results, such as the influence of process parameters on the properties of composite layers, are presented. A possibility of incorporating graphite particles into an anodic oxide layer structure has been demonstrated. The thickness and microhardness of the obtained layers and Al_2O_3 layers fabricated in identical conditions have been compared.

Key words: *composite; aluminium oxide; graphite; scanning microscopy; X-ray diffraction*

1. Introduction

Improvement of mechanical properties of operational materials more and more frequently consists in modifications within the surface layer. Materials characterized by a smooth change of properties from the core to the surface seem to be the best technological solution for upper layers. The inner layer directly adhering to the substrate is supposed to ensure maximum adhesion, while the upper layer is to preserve optimal tribological properties. In the case of modified layers and multilayers produced from materials with intermediate properties superimposed one onto another, this dependence is fulfilled. At present, such layers are produced in multiple technological processes. Layers obtained from composite materials, usually produced by electrochemical methods, are a combination of two or more separate and mutually insoluble phases and collectively they ensure better properties than those of each individual material. If composite layers showed a smooth change of properties from the core to the surface and if they could be obtained in a single, inexpensive process, they would become competitive for intermediate and modified layers, due to a shortened production time and reduced production costs.

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Oxide coatings produced electrolytically on aluminium alloys are characterized by very high adhesion to the substrate, making their detachment impossible, and typical porosity of their surface enables sorption of other substances. An advantage of the oxide layer production is the possibility of manipulating its mechanical properties. As a result of changes in the current density and electrolyte temperature, the thickness, porosity and microhardness of the layer change as well [1, 2]. Increased porosity of the oxide layer entails an increased amount of substances absorbed. Both the oxide layer structure and the above-mentioned dependences predispose oxide coatings to serve as matrices for composite layers [3, 4].

By changing the nature of the reinforcing phase in the aluminium oxide matrix, we can use the composite layer in a number of ways. Obtaining a composite material in the form of an abrasion-resisting aluminium oxide matrix enriched with a lubricant, would allow us to obtain an upper layer with good tribological properties. One of the most frequently employed lubricants is graphite whose structure is composed of parallel carbon planes, interlinked by weak van der Waals bonds. A specific crystal structure and low hardness (ca. 1 in Mohs' scale) of the graphite lamellar structure account for its excellent lubricating properties.

The above-mentioned properties have inspired the authors of this paper to research into the possibility of incorporating graphite in the aluminium oxide structure during a hard anodizing process, being the only technological treatment when forming a composite oxide layer.

2. Experimental

All layers were fabricated via hard anodizing method on a substrate made of PA2 alloy (AlMg2). The choice of the alloy was dictated by its easy oxidation and good results of previous studies. The process was preceded by purifying the sample surfaces and degreasing through etching in a 5% KOH and a 10% HNO_3 solutions. The surfaces so prepared were subject to electrolytic oxidation by the direct-current method, using a stabilized GPR-25H30D feeder cable. The electrolysis was conducted in an electrolytic tank of the dimensions: 18×18 cm^2. The foundation of the electrolyzer was in the shape of a square with rounded edges. Electrodes were immersed to the depth of 3 cm from the tank bottom and 3 cm from the electrolyte surface. A 45×17 mm^2 plate made of AlMg2 alloy was used as the anode and a lead plate of the same dimensions was used as the cathode.

The electrolytes constituted water solutions of sulfuric, oxalic and phthalic acids (SFS) for the Al_2O_3 layer formation and water solutions of the same acids with an addition of loose graphite for the production of composite layers. During the anodizing process, the electrolyte was stirred in one direction with a mechanical stirrer at the constant speed of 150 r.p.m. This stirring speed enabled obtaining a homogeneous graphite suspension throughout the electrolyte volume. An addition of the phthalic acid to an electrolyte ensures obtaining layers with the largest possible pores, as well as conducting the process at room temperature [6, 7]. The purity degree of the graphite used as an addition to the electrolyte-base amounted to 99%, with the average size of grain being smaller than 1 μm. Due to the aluminium oxide nanopore size, graphitization was conducted during the electrolysis, producing a composite layer achieved by incorporating graphite into the oxide structure. The anodizing process was conducted during a constant time period of 1 h, at the current density of 2 or 3 A/dm^2, and electrolyte temperatures of 293 and 303 K. The oxidation conditions for particular samples are summarized in Table 1.

Table 1. Parameters of the anodizing process

Sample	Anodic current density [A/dm^2]	Electrolyte temperature [K]	Electrolyte composition
4A	2	293	SFS + graphite
4B	3	293	SFS + graphite
4C	2	303	SFS + graphite
4D	3	303	SFS + graphite
4A1	2	293	SFS
4B1	3	293	SFS
4C1	2	303	SFS
4D1	3	303	SFS

After completion of the anodizing process, the samples were rinsed for 1 h in distilled water in order to remove remaining electrolyte. The thickness of all layers was measured with a Fischer's Dualscope thickness gauge, by making 10 measurements along the sample length. The Dualscope instrument works based on the current-rotational method, with its maximum error amounting to 1 μm. The structure and surface morphology were examined using a Philips XL30 scanning microscope. No tests were conducted on the composite layer microsections, since their mechanical preparation caused rinsing out of graphite from the oxide layer. Therefore, the analysis of the compositions of the layers was performed using an X-ray diffractometer by the standard method with the use of a Philips PW3710 X-ray diffractometer and the X'PERT computer program. The angular range 2θ of the diffractograms was 5–85° or 5–110°. The substrates of the samples, made of an aluminium alloy with small admixtures of Mg, Mn and Ti, as well as graphite used as an addition to the electrolyte, were subject to the diffractometric analysis. On the layer transverse microsections, within a distance of 15 μm from the substrate, indentations were made with the use of a Hanemann microhardness tester, by applying 0.3 N load. Microhardness was determined based on the photos of microsections taken with a Neophot 21 microscope.

3. Results and discussion

During the oxidation process at a constant current value, measurement of anodizing voltage was made, the value of which was varying with a growing oxide layer. At the beginning of the process, the voltage increased to a certain maximum value, called critical voltage; next, it decreased slightly and having reached a certain minimum, increased again. The reason for this phenomenon are processes taking place during the oxide coating's formation. The value of voltage was found proportional to the current density, and inversely proportional to the electrolyte temperature.

An examination conducted with a scanning microscope showed a structural architecture typical of oxide layers produced on aluminium alloys. Figure 1 illustrates a columnar-fibrous structure; the fibres are perpendicular to the sample surface. The surface porosity visible in Fig. 2 is the effect of oxide cellular structure, formed as a result of the electrolyte dissolving activity, which occurs in consequence of an increasing solution concentration under the influence of current flow in sites of breakdown.

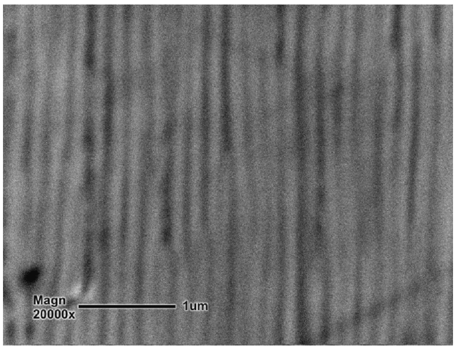

Fig. 1. Structure of the oxide layer obtained at 293 K and current density of 2 A/dm^2

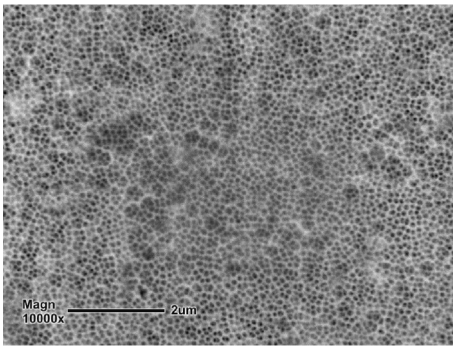

Fig. 2. Morphology of the oxide layer surface obtained at 293 K and current density of 2 A/dm^2

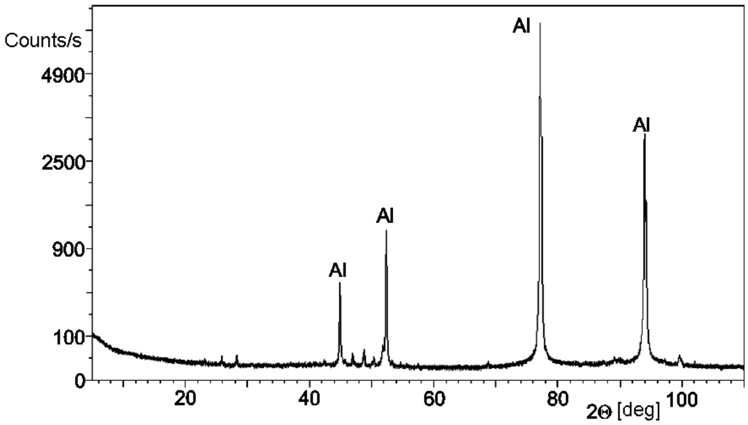

Fig. 3. X-ray diffractogram of the AlMg$_2$ alloy

On the X-ray diffractograms of the substrate and layers of Al_2O_3 + graphite, shown in Figs. 3–5, strong reflexes are visible, in major part belonging to Al, as well as a number of weak reflexes corresponding to alloying additions and graphite. The depth of X-radiation penetration depends on the type of the matter studied and fluctuates between 0.5 and 2 mm. The thickness of the Al_2O_3 + graphite layers fluctuated within the range of 29–41 μm, which constitutes a fraction of the studied sample percentage volume and therefore, the X-radiation penetrated too deeply, thus giving the image of the material from the sample's entire thickness range. In consequence, the reflexes corresponding to graphite are very weak and have a small number of counts. In all cases, a rise in the diffractogram background can be observed in the 2θ range of 20–45°. A rise in the diffractogram background within the above-mentioned angular range is characteristic of the amorphous Al_2O_3 layer, which does not give any reflexes. The minimum of the amorphous "hump" in the layers examined falls on the *d* value 3.22–3.24 Å.

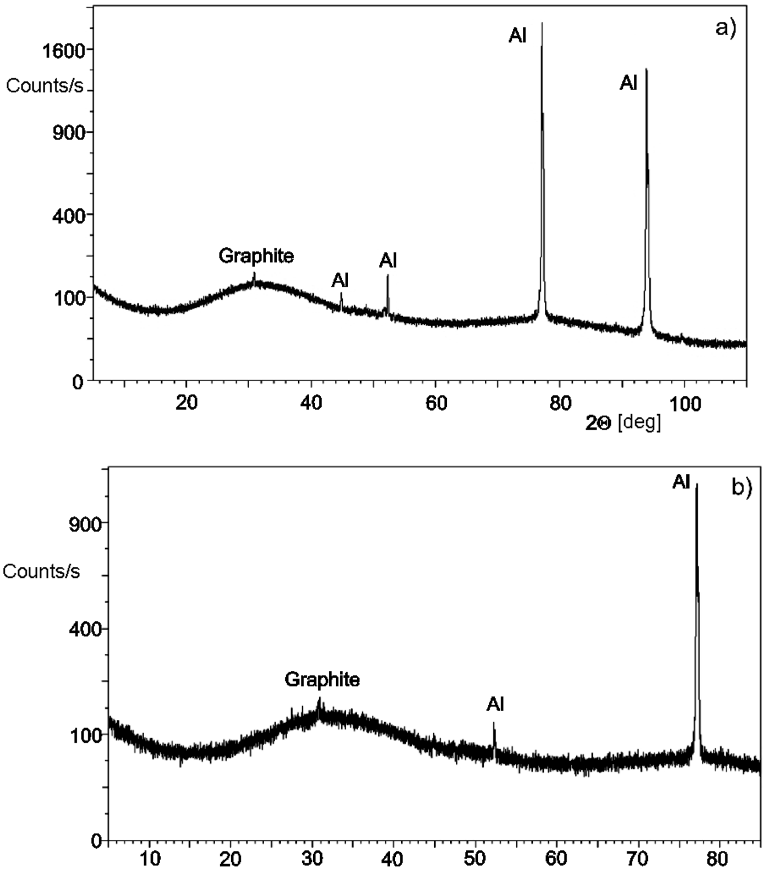

Fig. 4. X-ray diffractograms of the composite layers for samples: a) 4A, b) 4B

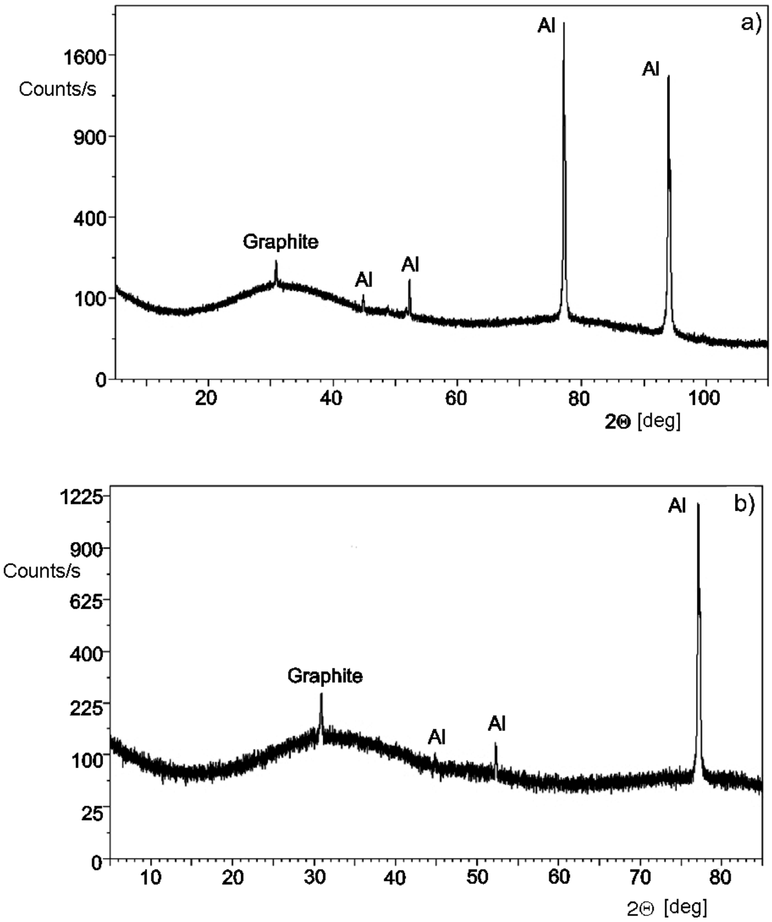

Fig. 5. X-ray diffractograms of the composite layers for samples: a) 4C, b) 4D

The diffractogram in Fig. 4a is dominated by two intense peaks 1.435 Å and 1.223 Å, and a few weak ones, originating from the sample substrate. The only peak belonging to graphite 3.363 Å is characterized by 41 counts/s, which testifies to a small amount of graphite. The diffractogram in Fig. 4b resembles the above-mentioned one. Reflexes 2.342 Å, 2.047 Å, 2.029 Å and 1.435 Å belong to the sample substrate, while the reflex 3.365 Å belongs to the graphite with 41 counts/s. On the diffractogram in Fig. 5a, two strong reflexes, 1.434 Å and 1.223 Å, are visible as well as a few weak reflexes belonging to the sample's substrate. Graphite is marked by one peak 3.362 Å with 82 counts/s, therefore the amount of graphite absorbed into the oxide layer is twice larger than in the two previous samples. The diffractogram in Fig. 5b is similar to those described above. A few weak reflexes and one strong, 1.435 Å, belong to the substrate, whereas the reflex 3.361 Å belongs to graphite, with the number of counts amounting to 116 counts/s, which indicates the largest amount of graphite in the Al_2O_3 layer among the investigated surfaces.

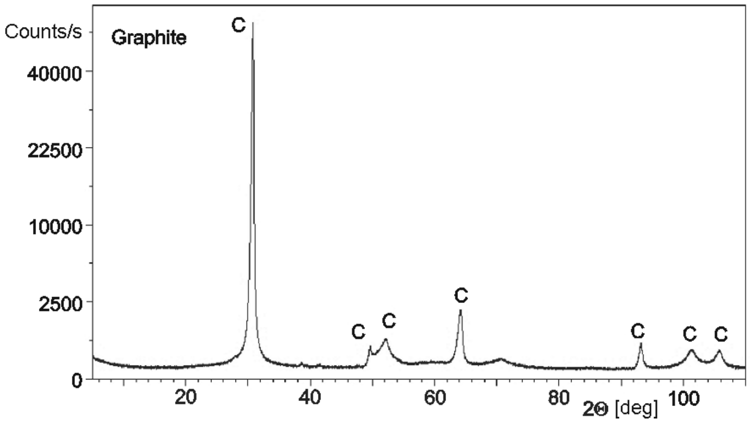

Fig. 6. X-ray diffractogram of graphite

Figure 6 presents a diffractogram of loose graphite. The basic reflex 002, whose value amounts to 3.367 Å and the intensity $I = 100$ achieved a very large number of counts, i.e. 53580 counts/s. This graphite belongs to the polytypic 2H type. The value of reflex 3.367 suggests that we have to do with hexagonal graphite with good lubricating properties.

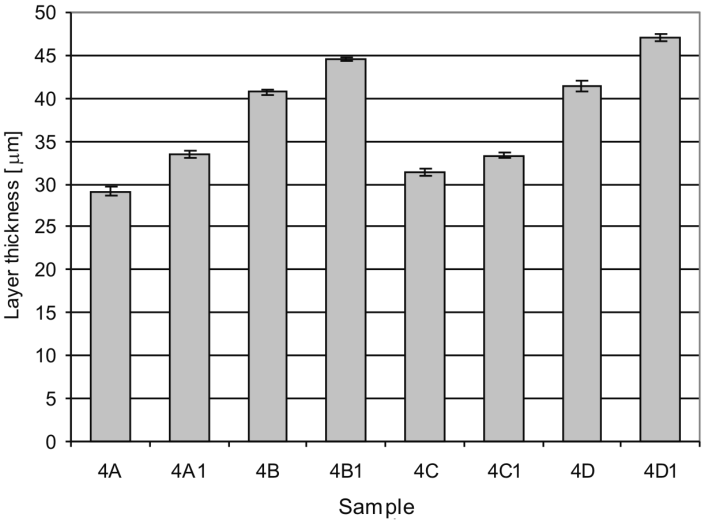

Fig. 7. Influence of current density, electrolyte composition, and temperature on the thickness of the layers produced

As results from the diagram presented in Fig. 7, the values of anodizing voltage, connected with the current density and temperature and composition of electrolyte, have a direct influence on the coatings thickness during the anodizing process. The current density and the electrolyte composition have a decisive influence on the layer thickness. The influence of electrolyte temperature is scanty, with differences ranging within the error margin of the measuring instrument and a standard deviation. Both, the homogeneity of the oxide layer substrate and the method of the anodizing enabled us to obtain the layers of uniform thickness throughout the sample surface.

Thickness of the Al_2O_3 + graphite layer formed at 293 K amounted to 29.1 μm at 2 A/dm^2 current density and 40. 7 μm at 3 A/dm^2, while at 303 K, it amounted to 31.4 μm at the current density of 2 A/dm^2 and 41.5 μm at 3 A/dm^2 . The thicknesses of Al_2O_3 were was by 6–13% higher than those of composite layers, which results from a better access of the electrolyte ions to the oxidized material.

Microhardness is one of the basic properties connected with the upper layer strength and resistance to wear. Microhardness of oxide layers formed on Al alloys depends on the conditions of the anodizing process, decreasing upon increasing the surface porosity. Based on Fig. 8, it can be concluded that all layers formed in the electrolyte containing graphite have higher microhardness than those formed in the basic electrolyte. The difference in microhardness between the Al_2O_3 layers and the Al_2O_3 + graphite layers varies between 149 and 524 MPa, depending on the current conditions and electrolyte temperature. The nature of changes in microhardness depends mostly on the electrolyte temperature. At of 293 K the layers had higher microhardness during anodizing at current density of 2 A/dm^2, whereas at 303 K the layers had higher microhardness during anodizing at current density of 3 A/dm^2. The above dependences imply that filling of the aluminium oxide fibrous structure results in its enhanced hardness.

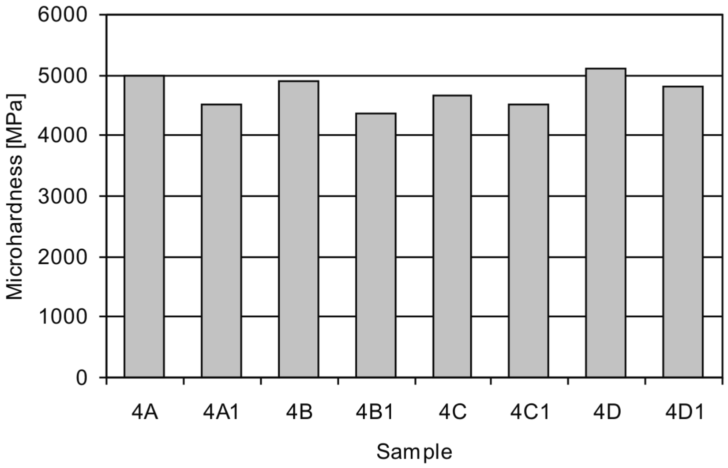

Fig. 8. Effect of anodizing conditions on microhardness of oxide and composite layers

From the difference in size of graphite grains and oxide nanopores it results that the mechanism of obtaining a composite layer consists in simultaneous building-in of graphite grains into the structure of oxide layer during its formation. Figures 9 illustrate the relations between the anodizing voltage and the process duration for Al_2O_3 layers and for Al_2O_3 + graphite layers.

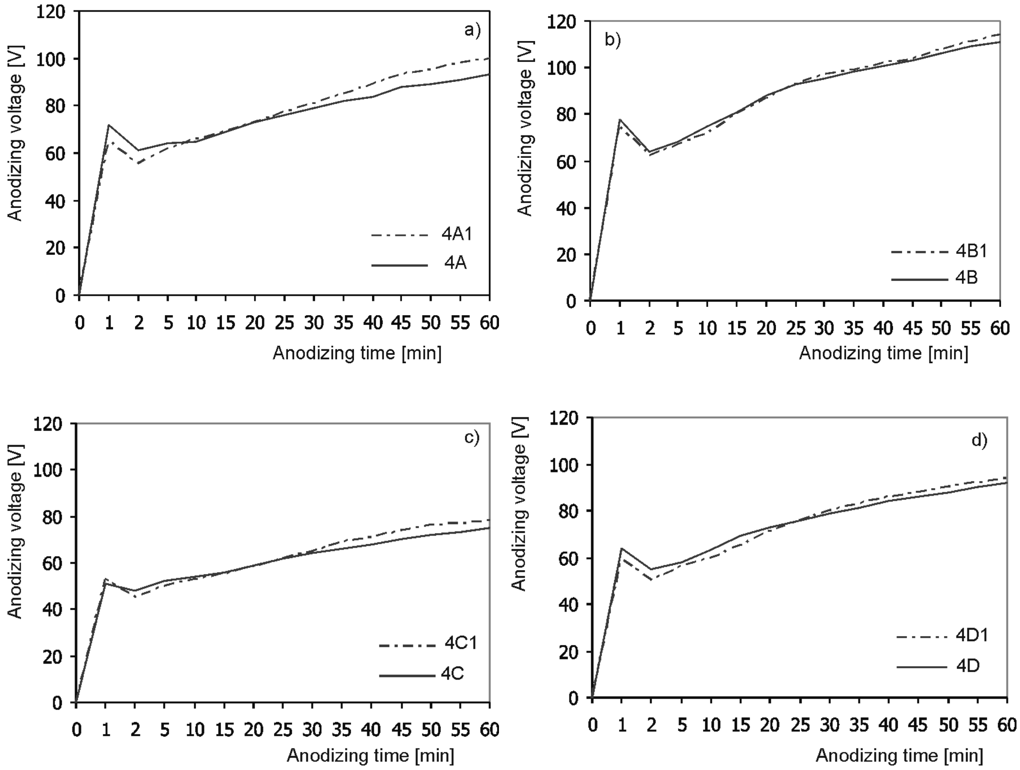

Fig. 9. Relations between anodizing voltage, time of process and composition of electrolyte and temperature for samples: a) 4A1, 4A, b) 4B1, 4B, c) 4C1, 4C, d) 4D1, 4D

During the formation of the Al_2O_3 + graphite layer, the initial anodizing voltage is higher than that of the Al_2O_3 layer. This dependence is connected with partial restriction of access of O^{2-} ions from the electrolyte to the alloy surface, caused by graphite particles. Consequently, growth of the composite layer is slower than that of the Al_2O_3 layer, which in turn results in lower resistance and lower anodizing voltage of the layerin further stages of the process.

4. Conclusions

The developed technology enables obtaining composite layers of aluminium and graphite oxide during one technological process. The largest amount of graphite in the Al_2O_3 layer was obtained at the current density of 3 A/dm^2 and electrolyte temperature of 303 K. Al_2O_3 + graphite composite layers of a smaller thickness, from 6 to 13% have higher microhardness of 3 to 10% when compared to the Al_2O_3 layers fabricated in the same conditions. At 293 K the layers have higher microhardness after anodizing at the current density of 2 A/dm^2, whereas at 303 K the layers had higher microhardness during anodizing at the current density of 3 A/dm^2.

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