

ANALYSIS OF Al_2O_3 LAYERS MORPHOLOGY AND MICROSTRUCTURE

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The paper presents the characterization of obtaining Al_2O_3 oxide layers on aluminium AlMg₂ alloy as a result of hard anodizing by the electrolytic method in a three-component electrolyte. The Al_2O_3 layers obtained on the AlMg₂ alloy in the three-component SBS electrolyte were subjected to detailed microstructural investigations (by means of a scanning electron microscope, SEM). By applying X-ray diffraction, examination of the obtained oxide layers phase compositions was carried out. It was found that the Al_2O_3 oxide layers obtained via hard anodizing in a three-component electrolyte are amorphous. The chemical composition of the Al_2O_3 layers is presented and compared to the results of stoichiometric calculations for the Al_2O_3 layer. Surface morphologies of the obtained oxide layers are characterized and discussed in nano- and microscopic scales. The surface morphologies of the layers obtained have a significant influence on their properties, including their susceptibility to further modification (e.g. to incorporation of graphite), their wear resistance and the capacity for sorption of lubricants.

Keywords: *nano- and microstructure, surface layer Al_2O_3 , surface characterization, scanning electron microscopy (SEM), X-ray diffraction.*

According to many authors [1–3] one of the most important research directions in the field of new constructional materials in machine building are materials resistant to operation at high temperatures (above 1000°C). Such materials will be necessary for, e.g., car engines of new type, which must meet new requirements concerning fuel consumption. Most probably, these will be ceramic materials or materials covered with special coatings.

A characteristic feature of ceramic materials is their insignificant wear and a low friction coefficient when co-working with other materials in the presence of a lubricant. The most recent world trends in the machine building sector, in particular with reference to piston machines, are heading to reduce their lubrication and cooling. A question arises then, what the upper layer of a ceramic material should be like in order to maintain the low wear and frictional resistance.

The Al_2O_3 layers belong to ceramic layers and, in the opinion of many authors who deal with the problems of upper layers, the nearest era of future construction materials will belong to ceramic materials. One of the most popular ceramic materials is the aluminium oxide Al_2O_3 which, with the development of technology, has found a number of new application areas over the past years. Ceramic materials have physicochemical properties which predispose them to a vast range of applications in structures working at high temperatures, i.e. in combustion engines, gas turbines and piston compressors.

The possibility of covering aluminium and its alloys with oxide coatings has resulted in an enhanced application of these materials, especially for:

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- components of couplings, transmissions, guides and slide ways;
- components in automatics and hydraulic controllers;
- rolling bearing races in a couple: steel – Al₂O₃;
- engine pistons and compressor cylinders sliding surfaces.

Experimental procedure. A new significant problem (due to the possibility of shaping materials properties in a wide range) is the oxide layer on aluminium obtained by means of hard anodizing. The basis for the hard anodizing of aluminium is the fact that the coating is formed at the expense of mass decrement of the substrate which turns into the Al₂O₃ compound.

The electrolytic processes of obtaining oxide layers on aluminium are conducted in electrolyte solutions which partly dissolve the layer being formed. Therefore, an essential amount of the electric energy consumed for the production of an oxide layer on aluminium surface will not actually correspond to the theoretical calculations.

The most widespread method so far has been anodic coating in a sulfuric or oxalic acid at lowered temperatures, from –10°C to +5°C, depending on the type of electrolyte. This required the erection of necessary installations to lower the electrolyte temperature for surface treatment which was connected with high capital expenditure. Therefore, researches on anodizing at elevated temperatures have been conducted for years. The purpose of the researches is to apply such electrolyte that would make it possible to obtain hard oxide layers at room temperatures. Elimination of the electrolyte cooling stage would considerably reduce the cost of oxide coatings production. It would be possible if hard anodizing is conducted at temperatures of 20...40°C and higher.

At the same time coatings with better properties could be obtained owing to the Al₂O₃ oxide phase transition at a temperature of 20°C. An increase in temperature accompanying the oxidation process is conducive to etching aluminium oxide fibers. In consequence, an oxide cell of a more regular (ideal) structure is formed [4–7]. The increasing electrolyte temperature has also an effect on the oxide coating porosity [1, 4, 8]. Porosity of the obtained oxide layers is of major importance for their utilization for sliding cooperation with plastic materials.

The anodizing method developed by the author does not require cooling and the process heat is used for controlling the properties of the oxide layers obtained. Controlling of anodizing parameters allows, within some limits, programming the selected functional properties of future upper layers [3–4]. According to the method proposed, oxidation is conducted in a three-component water electrolyte. Hard anodizing was conducted in a three-component electrolyte called SBS, consisting of: sulfuric acid – H₂SO₄; oxalic acid – (COOH)₂; succinic acid – (CH₂)₂(COOH)₂.

The process control factors are: current density – 2...4 A/dm²; temperature of electrolyte – 293...313 K; oxidation time – 20...80 min.

Before the anodic oxidation process, the surfaces of specimens were ground with abrasive papers of different gradation, always using the same technology, in order to obtain an identical accuracy class for the precoat (irregularities height $R_a = 0.75 \pm 0.15 \mu\text{m}$).

Results and discussion. Microstructure and morphology of Al₂O₃ layers surfaces. The structure of oxide layers is one of the main factors determining their chemical, physical, surface and mechanical properties. Therefore the control of the structure of oxide layers of Al and its alloys is very important for the electrolytic

method of producing some machine parts. In this connection the knowledge of the formation mechanism of oxide layers obtained via the hard anodizing method is essential.

Examination of the microstructure and morphology of Al_2O_3 oxide layers obtained via hard anodizing was conducted using a scanning electron microscope, Philips X130/ESEM/EDAX.

Based on the outcomes of the research on obtaining oxide layers on aluminium in the first few seconds of electrodeposition, it can be affirmed that the initially active places are roughness peaks of the substrate metal surface and crystal ribs as well as the places with crystal lattice deformations and other defects of the anode surface.

The effect of the oxide layer growth during the first several seconds of anodizing is the formation of structure of dendrites. A conclusion can be drawn based on this investigation that the size and quantity of substrate metal crystals, as well as their form and orientation, i.e. their mutual arrangement, are of decisive importance for obtaining the oxide layer final structure. The more are the substrate metal crystals with a given growth direction in relation to the total number of crystals, the higher is the orientation degree or the texture improvement degree in the oxide layer obtained. So, it can be concluded that both the texture and the crystal size are important factors, determining the properties of an oxide layer obtained via hard anodizing.

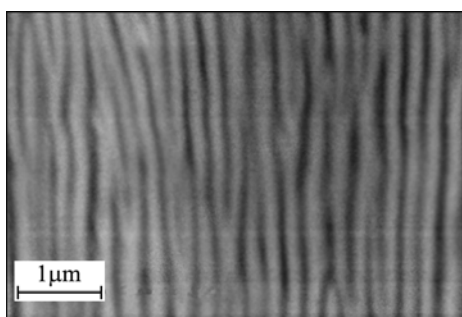


Fig. 1. Columnar (fibrous) structure of the Al_2O_3 layer.

The next stage of the layers formation mechanism is transformation of the dendritic structure into a columnar (fibrous) one. Such transformation takes place as a result of the applied electric field which is directed from the anode to the cathode and as a result of another factor, i.e. the abstraction direction of the heat emitted very intensively in the oxide layers growth regions. The formed columnar (fibrous) structures, oriented as a result of the electric field influence and the heat abstraction direc-

tion from places of oxide layers growth (substrate), are presented in Fig. 1.

The structure of oxide layers depends, to a large degree, on the type and concentration of electrolyte as well as on the conditions in which the hard anodizing process is conducted. The anodic density of current applied during the electrolytic process has a significant influence on the structure of anodic oxide coatings. It influences the process speed which is strictly correlated with the growth and size of crystals in the coating. Also, the temperature of electrolyte affects the formation of coatings of a different grain size, which results from changes in the conditions of secondary oxide dissolution.

The investigation results of the morphology of Al_2O_3 layers obtained via hard anodizing are presented in Figs. 2.

Chemical and phase compositions of Al_2O_3 layers. The analysis of the chemical composition of the Al_2O_3 layers obtained via the electrochemical method in a three-component SBS electrolyte was conducted using a scanning electron microscope Philips X130 with an EDS attachment. The analysis of the chemical composition of the Al_2O_3 layer on a transverse microsection has shown that only in

the central zone, according to thickness, the chemical composition corresponded to the stoichiometric calculations. The chemical composition measurements carried out in the middle part of the layer showed 52.93% aluminium content and a 47.07% oxygen content. According to the stoichiometric calculations, the Al_2O_3 layer should have the following chemical composition: 52.92% Al and 47.08% of oxygen.

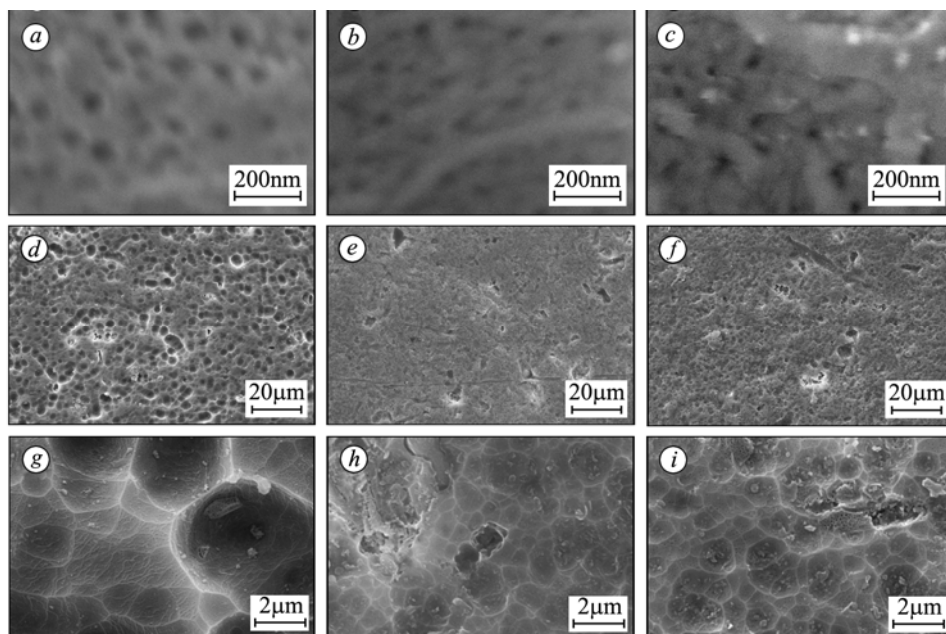


Fig. 2. Nanopores (*a-c*), micropores (*d-f*) and developed morphology (*g-i*) of the Al_2O_3 layer obtained via hard anodizing: *a* – $j = 2 \text{ A/dm}^2$, $t = 60 \text{ min}$; *b* – $j = 4 \text{ A/dm}^2$, $t = 40 \text{ min}$; *c* – $j = 4 \text{ A/dm}^2$, $t = 60 \text{ min}$.

Results of the chemical composition analysis of the Al_2O_3 layer in the middle zone are presented in Fig. 3. According to the conducted research, when approaching the Al substrate, the content of oxygen decreases and the Al content grows, whereas when receding from the metal substrate, the oxygen content in the layer increases and the Al content decreases. The research results regarding the changes in oxygen and aluminium contents along the Al_2O_3 layer thickness are shown in Fig. 4.

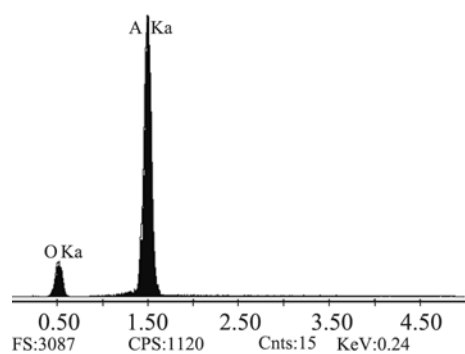


Fig. 3.

Fig. 3. Results of the Al_2O_3 layer chemical composition analysis.

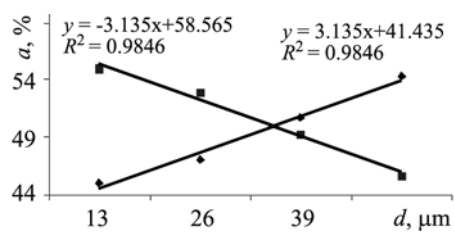


Fig. 4.

Fig. 4. Change in oxygen and aluminium contents across the Al_2O_3 layer thickness: \blacklozenge – O; \blacksquare – Al.

A DRON-2 diffractometer was used for the X-ray phase analysis of the obtained Al_2O_3 layers. The X-ray diffractogram of the Al_2O_3 layer obtained on a crystalline AlMg_2 aluminium alloy is presented in Fig. 5. All diffraction reflexes in the figure originated from the metal substrate. The X-ray phase analysis has shown that the obtained Al_2O_3 layers are amorphous.

Measurements of the Al_2O_3 layers microhardness done on transverse microsections have shown that as the oxygen and aluminium contents change, the microhardness (μHV) decreases. Examination of the layers microhardness was conducted using a Neophot 2 microscope with a Hanemann's attachment (microhardness tester).

The results of distribution of the Al_2O_3 layer microhardness according to the thickness are presented in Fig. 6.

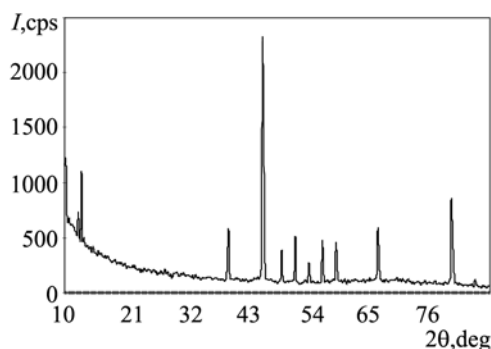


Fig. 7.

Fig. 7. X-ray diffraction pattern of oxide layer.

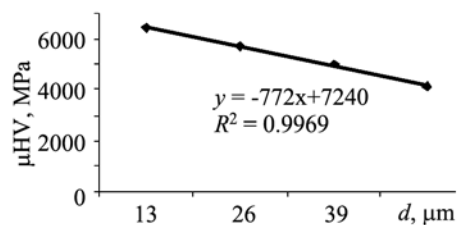


Fig. 8.

Fig. 8. Distribution of the Al_2O_3 layer microhardness according to the thickness: \blacklozenge – μHV .

CONCLUSIONS

On the basis of the researches on the morphology of the nano- and micro-structure, the chemical composition and phase composition of Al_2O_3 layers obtained on the AlMg_2 aluminium alloy via hard anodizing in a three-component SBS electrolyte, as well as using the theoretical analysis results, it can be concluded that:

- the Al_2O_3 layers obtained on the AlMg_2 alloy as a result of hard anodizing are completely amorphous;
- the Al_2O_3 layers obtained as a result of hard anodizing have a fibrous structure of amorphous layers;
- the Al_2O_3 layers obtained in the SBS electrolyte have a chemical composition similar to the stoichiometric calculations for Al_2O_3 ;
- the Al_2O_3 layers have a developed surface morphology being the result of a fibrous structure (the effect of which are the nanopores formed at the contact points of aluminium oxide fibers) and of the secondary dissolution of electrolyte as well as energetic interferences (micropores being the effect).

РЕЗЮМЕ. Описано спосіб отримання оксидних покриттів на основі Al_2O_3 , сформованих на підкладці сплаву AlMg_2 анодуванням у трикомпонентному електроліті. Мікроструктурні особливості шарів Al_2O_3 досліджено за допомогою сканівного електронного мікроскопа (SEM). Для вивчення фазового складу покриттів використовували рентгенодифракційний аналіз. Виявлено, що оксидні покритви з Al_2O_3 , отримані анодним оксидуванням у трикомпонентному електроліті, аморфні. Подано хімічний склад покриттів та порівняно його з результатами стехіометричних обчислень. Проаналізовано морфологію поверхні оксидних покриттів та обговорено їх поведінку на нано- та макрорівнях. Морфоло-

гія поверхні суттєво змінює інші властивості, зокрема, їх здатність до подальшої модифікації (включення графіту), зносотривкість та схильність до сорбції компонентів мастил.

РЕЗЮМЕ. Описан способ получения оксидных покрытий на основе Al_2O_3 , сформированных на подкладке сплава $AlMg_2$ анодированием в трехкомпонентном электролите. Микроструктурные особенности слоев Al_2O_3 исследовано с помощью сканирующего электронного микроскопа (SEM). Для изучения фазового состава покрытий использован рентгенодифракционный анализ. Обнаружено, что оксидные покрытия из Al_2O_3 , полученные анодным оксидированием в трехкомпонентном электролите, аморфны. Наведен химический состав покрытий и сравнено его с результатами стехиометрических расчетов. Проанализирована морфология поверхности оксидных покрытий и обсуждено их поведение на нано- и макроуровнях. Морфология поверхности существенно изменяет другие свойства, в частности, их способность к дальнейшей модификации (включения графита), износостойкость и склонность к сорбции компонентов масла.

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Received 30.04.2008