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Effect of the base material condition on the structure and properties of Al_2O_3 oxide layers

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The paper presents a new method for modelling oxide layers for tribology related needs. The most recent world trends in the machine-building sector, in particular with reference to piston machines, are heading towards reducing their lubrication and cooling. Hence, a question arises, what the upper layer of a ceramic material should be like in order to maintain low wear and low frictional resistance. An oxide layer for tribological needs has been formed on an $AlMg_2$ alloy as a result of hard anodizing in SAS electrolyte. This electrolyte enables the control of oxide layer production parameters, which allowed obtaining for the tests an oxide coating with a wide range of changes in porosity and micro-hardness µHV. Anodizing has been carried out by means of the direct-current method, using a stabilized feeder, GPR-25H30D, for a constant electrical charge density of 180 $Amin/dm^2$. A lead plate has been acted as the cathode in the anodizing process. By means of a scanning electron microscope (SEM), the surface morphology and structure, and the chemical composition of the layers have been analyzed.

Keywords: Oxide layers Al_2O_3, Nanostructure, Nanopores, SEM

1 Introduction

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 mechanism of formation and growth of oxide layers obtained via the hard anodizing method is essential. 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's surface, as well as the places with crystal lattice deformations and other defects of the anode surface[1-3].

The effect of growth of an oxide layer during the first several seconds of anodizing is the 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's final structure. The more crystals of the substrate metal with a given growth direction in relation to the overall number of crystals, the higher the orientation degree or the texture improvement degree in the oxide layer obtained. It can be concluded from the above presented issue that both the texture and the crystal size are important factors determining the properties of an oxide layer obtained via hard anodizing. The next stage of the layers' formation mechanism is the 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 direction of abstraction 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 direction from the places of oxide layers' growth (substrate), are presented in Fig. 1.

Depending on the conditions of electrodeposition and the substrate material quality, it is possible to obtain a coarse fibrous or fine fibrous structure of the oxide layer. Thus, it is possible to obtain oxide layers with a "compact" structure of reduced porosity and good anti-corrosion properties or with a "developed" structure of much higher porosity and completely different properties. A significant factor which influences the mechanism of oxide layers' formation and growth on aluminium and its alloys is adding of organic substances with surface-active properties to

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*Corresponding author (E-mail: Wladyslaw.Skoneczny@us.edu.pl) the electrolyte. Depending on the properties and concentration of such substances, the oxide layers obtained on the anode are more or less fine-fibrous, "compact", or vice versa. Under proper conditions, surface-active substances fully or partly cover the surface of the anode (on active places), as a result of which the secondary dissolution of the layer is considerably hindered. In consequence, the structure and properties of oxide layers will depend on the relative rate of adsorption of surface-active substances. The degree to which the electrolytic process is hindered depends on the surface concentration of the adsorbed particles and on the properties of the adsorbed layer[4-12].

2 Materials and Methods

Aluminium alloy $AlMg_2$ was used for the research. Specimens were cut out of a 1 mm thick sheet metal. In order to obtain an oxide coating of appropriate quality, and to avoid any irregularities in its structure, the surfaces of the specimens had to be correctly prepared before the oxidation process. For this purpose, they were subjected to mechanical surface treatment which allowed the elimination of different scratches and irregularities, and led to standardizing the surface of the prepared specimens. Initial preparation of the samples included etching in a 10% KOH solution and next, in a 10% HNO_3 solution. Aqueous solution of H_2SO_4, $C_2H_2O_4$ and $C_8H_6O_4$ was used as electrolyte. Anodizing was carried out by means of the direct-current method, using a stabilized feeder, GPR-25H30D, for a constant electrical charge density of 180 Amin/dm^2. A lead plate was the cathode in the anodizing process.

An oxide layer for tribological needs was formed on an $AlMg_2$ alloy as a result of hard anodizing in SAS electrolyte. This electrolyte enables the control of oxide layer production parameters, which allowed obtaining for the tests an oxide coating with a wide range of changes in volumetric porosity, i.e. 3.7/19 %, and in microhardness in the range from 330 to 510 μHV. Porosity and microhardness of the oxide layer is crucial for the good functioning of the sliding pair working in the couple: oxide layer – plastic material.

A scanning microscope (SEM) was used to produce images of the nanomorphology of Al_2O_3 layers' surfaces and the nanostructure of those layers from metallographic specimens. A magnification of 50 thousand times was used for surface analysis, which allows observation of the distribution of nanopores, while the magnification applied for the analysis of the structure was 20, 30 thousand times. The chemical composition of the oxide layers was also analyzed with the use of an EDS analyzer. Examination of the nanostructure and chemical composition of the obtained layers was carried out using a Philips X130 scanning electron microscope.

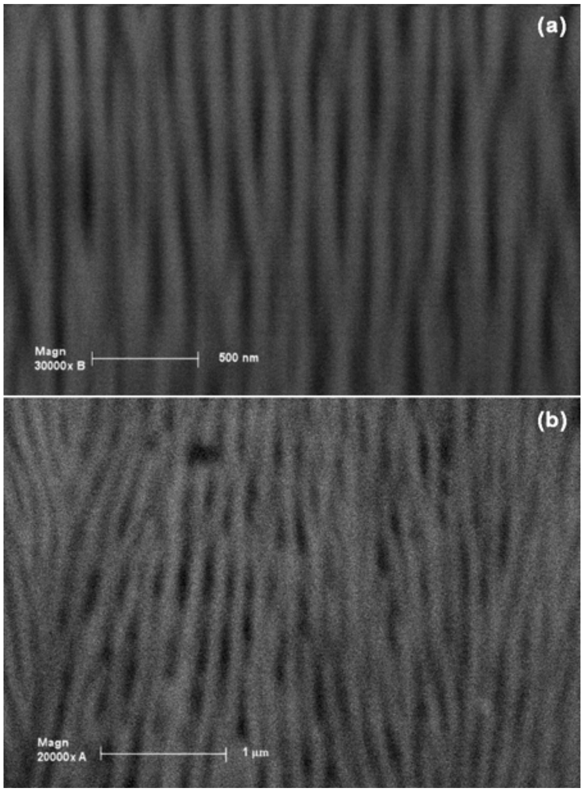

Fig. 1 — Nanostructure of the oxide layer: a) ideal Al_2O_3 layer, b) nanostructure of Al_2O_3 layer with undulated base material

3 Results and Discussion

Results of examination of the nanomorphology and chemical composition of the obtained oxide layers are presented in Figs 2, 3 and 4. Dimensions of the aluminium oxide fibres obtained in a three-component SAS electrolyte as well as the number of fibres and pores per mm^2 depend on the parameters of hard anodizing. All this has a very significant influence on the structure and properties of the oxide layers formed on a metal substrate in a specific condition.

Figure 1 presents oxide layers obtained on an $AlMg_2$ substrate, depending on the surface geometry characteristics: with surface undulation (b) and without substrate undulation (a). Deviations from the columnar structure of the oxide layer are visible, where whole groups of oxide fibres are directed at different angles, always oriented perpendicularly to the substrate. Such twisting of structural fibres of the oxide layer is the effect of the addition of admixtures to the substrate metal, and of local etching of grain boundaries by the electrolyte during electrodeposition. As a result of the so growing oxide layer structure, macropores appear between the oxide fibres which are formed as a result of the admixture in the metal substrate and etching of grain borders, as well as of roughness of the substrate. The issues discussed are visible in the photographs of the oxide layer surface (Fig. 2).

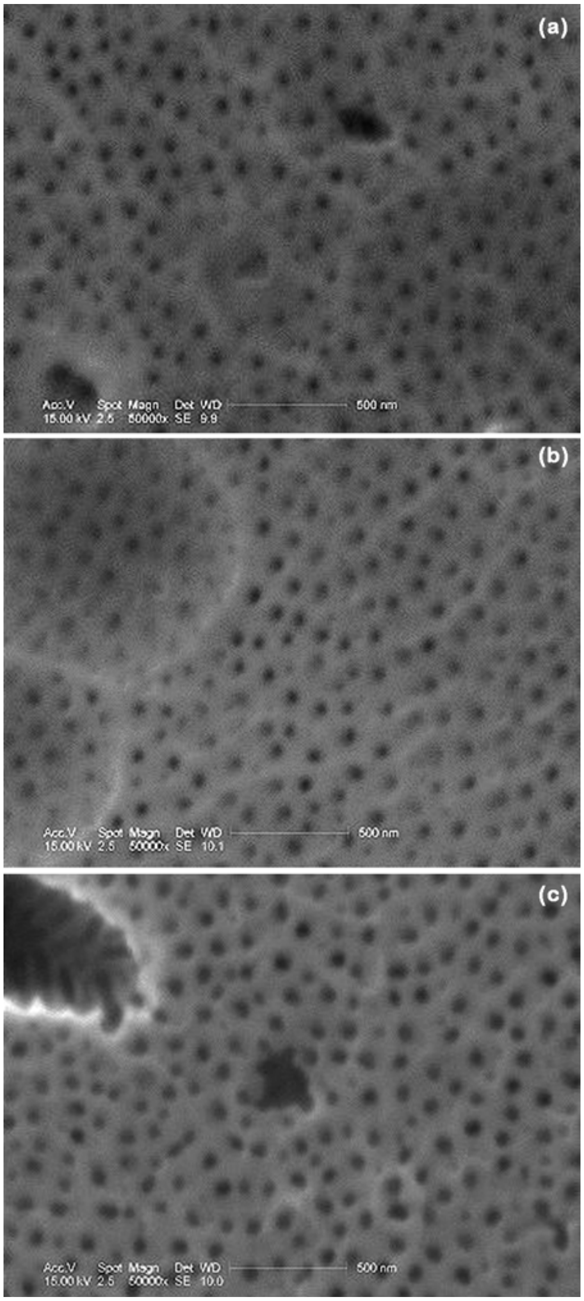

Fig. 2 — Morphology of surface with nano- and micropores in the oxide layer: a) compact structure, b) undulation effect, c) admixture effect

Functional properties of hard anodic layers can be modelled depending on the needs, already at the production stage. In the current practice, they have been applied in sliding pairs of technical objects operating under conditions of technically dry friction or limited lubrication, as well as conventional lubrication. In the first case, oxide layers cooperate with plastics containing film-forming substances (encouraging the production of a sliding film during use), e.g. PTFE, graphite or MoS2. Under conditions of limited and conventional lubrication, these films, after appropriate modification, work with cast iron piston rings or steel sliding surfaces of combustion engine cylinders. For each of these applications, a hard anodic coating with different properties must be produced. For the needs of lubricant-free sliding pairs,

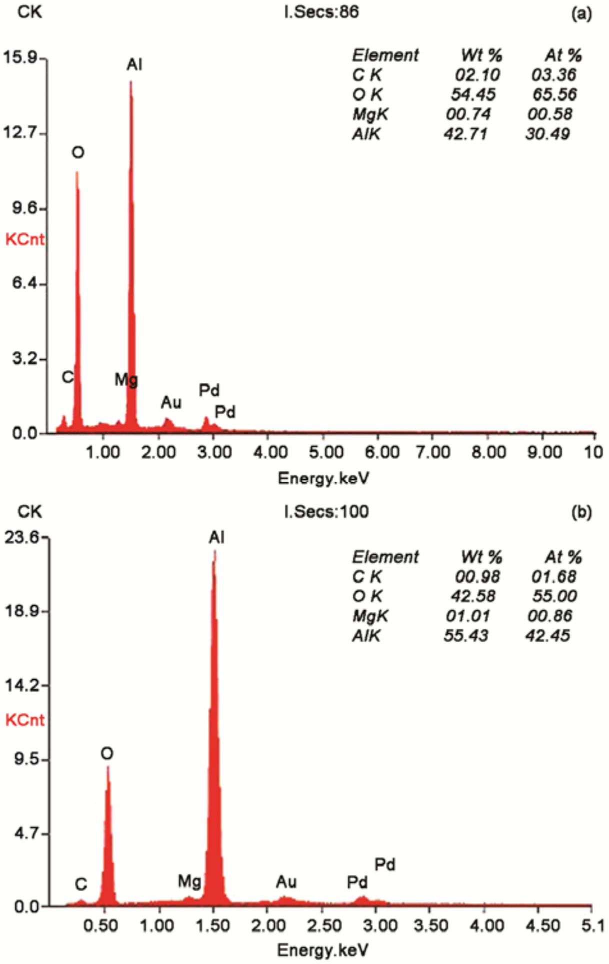

Fig. 3 — Changed in the chemical composition of Al_2O_3 layers: a) chemical composition at the surface, b) chemical composition at a ¼ distance from the surface

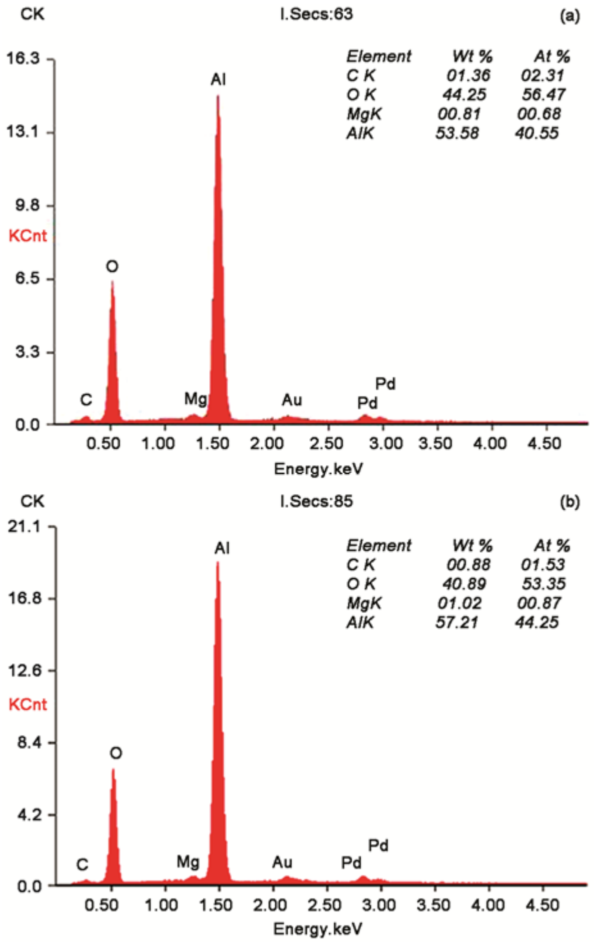

Fig. 4 — Changed in the chemical composition of Al_2O_3 layers: a) chemical composition in the middle of the layer, b) chemical composition at the substrate

oxides with low porosity and insignificant surface roughness are required. Sometimes, sealing of the coatings is applied before the cooperation. For the needs of lubricated sliding pairs, high porosity and modification with a chosen metal are required.

When operating under technically dry friction conditions, a plastic sliding film is formed on the oxide layer surface. The presence of such a film changes the nature of the cooperation from: plastic/oxide layer to plastic/plastic. In the process of friction of an oxide layer/polymer pair, the polymer material is transferred to the surface of the metal countersample. The process of polymer material transfer is quite complicated, as these particles may return from the countersample's surface to the surface from which they have been transferred. The polymer material particles, oscillating between friction surfaces, may combine and form aggregations which, as wear products, are expelled out of the friction zone. The transfer process is initiated by strong local adhesive tacking of friction surfaces. If cohesive values of the polymer material are exceeded, then its particles will appear on the countersample's surface. Further work of the surface will cause a situation where the transferred particles will be detached from the surface of the countersample, and local strong adhesive tacking will contribute to the transfer of next particles. The wear process is strictly bound up with the transfer process. In this way, a sliding film is formed.

Depending on the cooperation conditions, the transferred layer of the polymer material may by built from a material with a physical structure identical to that of the sample's material. The dynamics of the formation of the layer and its properties have a great impact on the tribological properties of sliding pairs. A polymer layer transferred to the surface reduces the roughness of the metal surface. Then, loads in contact areas decrease and the deformation of the polymer material in the upper layer is reduced.

Knowing the mechanism of the sliding interaction of the upper layer of an oxide coating with TG15 plastic, the manufacturing parameters can be selected in such a way that the range and intensity of destructive changes are as small as possible, which will result in obtaining their optimal durability and reliability during operation.

4 Conclusions

As results from the research presented, it is possible to obtain oxide coatings with predefined properties by appropriately modelling the parameters of their production. The microhardness and volumetric porosity of oxide layers obtained in three-component electrolytes make these coatings preferred for use in sliding couples.

The oxide layers obtained via hard anodizing on the $AlMg_2$ alloy have a fibrous structure, characteristic of amorphous layers. The oxide layers obtained in a SAS electrolyte on the $AlMg_2$ alloy have a columnar (fibrous) structure oriented under the influence of electric field. It is possible to maintain certain reservoirs on the surface of the oxide layer, e.g. lubricating, which are formed as a result of the development of the surface layer's porosity. The columnar structure of the oxide layer obtained on the $AlMg_2$ alloy may undergo certain disturbances (deviation from the ideal fibrous structure) as a result of various admixtures in the substrate metal.

When appropriate sliding parameters are selected, a sliding film is formed on the countersample with an oxide layer, which allows friction between the sample and the film with polytetrafluoroethylene (TG15 plastic), which reduces the friction process in the pair to a polymer/polymer pair. This is closely related to the knowledge of the properties of the materials used for sliding pairs.

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