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INFLUENCE OF THE NANOSTRUCTURE OF SURFACE CERAMIC COATINGS ON THEIR TRIBOLOGICAL PROPERTIES

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This study is an attempt of applying new electrolytes to obtain new generation oxide coatings. An oxide coating was deposited on aluminium Al(Al 99.5). The influence of an organic additive and anodizing parameters on the nanomorphology and nanostructure of the obtained coatings is described. The nanostructure and nanomorphology of oxide coatings were determined using a scanning electron microscope (SEM). An attempt was made to apply a new oxide coating for a sliding interaction with TGK 20/5 material. Tests were carried out under dry friction conditions. The friction coefficient was evaluated for the investigated sliding couple, as well as the intensity of wear of the specimens made of this material. The influence of the oxide coating nanostructure on the tribological properties of the tested couple was also determined.

Keywords: *nanostructure, oxide layers, hard anodising method, plastic, tribology.*

One of the basic problems in the continuously developing fields of engineering and technology is the manufacturing of high quality products with the production costs which are as low as possible. Therefore, an important factor which determines the method of forming parts of machines and devices is the manufacturing cost. The above-mentioned minimization does not, however, consist in the technological or organizational concentration of operations, but instead, in the design of a part which can be manufactured with the lowest possible number of operations or treatments, while simultaneously creating a surface coating with the required properties. Contemporary engineering and technology must satisfy at least the following requirements: manufacturing cost minimization, while maintaining the appropriate quality of the product; development of new engineering materials with consciously shaped properties; development of new engineering materials able to operate at high temperatures [1].

The meeting of these expectations requires intensive development of the methods of forming surface coatings. There are significant facts which support the usefulness of directing further research towards improvement of the existing properties of oxide coatings, thereby revealing the possibilities of applying them in the machine-building industry. The list of engineering materials presented in paper [2], shows that these will be ceramic materials and composites [2, 4] that shall predominate in the automotive industry in the future.

A characteristic feature of ceramic materials is their insignificant wear and 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 towards reducing their lubrication and cooling. Hence, the question arises of what the upper layer of a ceramic material should be like in order to maintain low wear and frictional resistance.

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

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tion, protective and decorative coatings, undercoatings; components of couplings, transmissions, guides and slideways; components in automatics and hydraulic controllers; rolling bearing races in steel–Al_2O_3 couple; engine pistons and compressor cylinders' sliding surfaces.

In order to strengthen the surface layer of aluminium alloys for cooperation sliding at high pressures (for example in lubricant free compressors) we use hard anoding.

The objective of the presented study is to determine the principal physico-mechanical and tribological characteristics of newly developed oxide coatings in interaction with the TGK 20/5 material, and to determine the usefulness of this couple for further operational tests which precede their potential implementation in lubricant-free compressors and pneumatic servo-motors.

Experimental details. Adding the organic substances with surface-active properties to the electrolyte has a significant influence on the mechanism of forming oxide coatings on aluminium. The mechanism of the influence of organic substances depends on the additive properties, as well as on the composition and properties of the electrolyte. A supposition can be made that under proper conditions the surface-active organic substances fully or partly cover the surface of the anode (on active places), as a result of which the oxidation of aluminium is considerably impaired. On the other hand, the adsorption of organic substances at the anode/electrolyte interface leads to holding up the secondary dissolution of the coating by the electrolyte. The role of this mechanism is performed by the addition of the above-mentioned organic acids.

The method developed does not require cooling, and the process heat is used for controlling the properties of the obtained oxide coatings. The control of the anodizing parameters allows, within some limits, programming the selected functional properties of the future surface coatings [5–10]. The above-mentioned method consists in oxidizing aluminium and its alloys in three-component electrolytes. An organic acid is added to the electrolyte mixture, composed of sulphuric and oxalic acids.

The first stage of the tests carried out as part of the study consisted in preparing the appropriate electrolytes and samples. The electrolytes, in which anodic oxidation was conducted at elevated temperatures, were based on sulphuric and oxalic acids. The following organic acids were marked out for the mixture of the above-mentioned components:

- electrolyte 1 – benzoic acid;
- electrolyte 2 – sebacic acid;
- electrolyte 3 – succinic acid;
- electrolyte 4 – glutaric acid;
- electrolyte 5 – cuberic acid.

Primary aluminium, A1(Al 99.5), was used for the tests. Specimens were cut out of a 1 mm thick sheet metal.

In order to obtain the 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 standardizing the surface of the prepared specimens. The test chart is presented in the Table.

The specimens with the highest and the lowest porosity were selected for the tribological tests.The sliding interaction between the produced oxide coating and counterspecimens proceeded in the conditions of technically dry friction; the unit pressure amounted to 0.1MPa, the average sliding speed was 1 m/s, and the area of the specimen contact with the counterspecimen was 1 cm^2.

The counterspecimens in the tribological tests were cylinders made of TGK 20/5 material (PTFE containing 20% graphite and 5% coke) with a cross-section area equal to 1 cm^2.

Parameters of forming oxide coatings

Type of electrolyte	Symbol Samales	Current density, A/dm^2	Temeprature, K	Time, min
1	A	2	293	40
	B	3	303	60
	C	4	313	80
2	D	2	293	40
	E	3	303	60
	F	4	313	80
3	G	2	293	40
	H	3	303	60
	I	4	313	80
4	J	2	293	40
	K	3	303	60
	L	4	313	80
5	Ł	2	293	40
	M	3	303	60
	N	4	313	80

Investigation of the tribological properties of the oxide coatings produced was conducted on the SDN measuring stand, constructed at the Department of Materials Science, University of Silesia (Fig. 1).

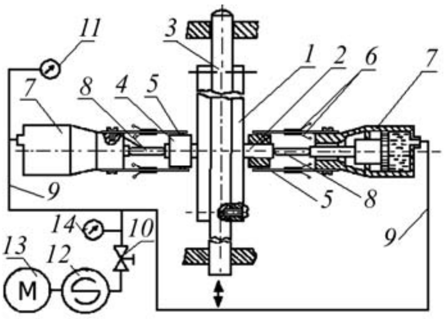

Fig. 1. Schematic of the SDN-set-up:
1 – specimen; *2* – counter-specimen;
3 – slide bar; *4* – frames; *5* – beam;
6 – strain gauges; *7* – hydraulic cylinder;
8 – joint; *9* – wires; *10* – regulator;
11 –manometer; *12* – pump;
13 – electric motor; *14* – manometer.

The value of wear was determined by weighing the counterspecimens before and after the sliding interaction. The counterspecimens were weighed after each stage of the interaction (every 96 km), using an analytical balance, WA 35, type TA 14, with a range of 100 g and accuracy of 0.01 mg. The friction coefficient value was calculated from the Amontons' formula.

Results and discussion. Results of examination of the nanomorphology and nanostructure of the obtained oxide coatings are presented in Fig. 2. The examination was conducted using a Philips X130 scanning electron microscope.

A model of the structure of the oxide coating produced by hard anodizing in three-component electrolytes is presented in Fig. 3 [5].

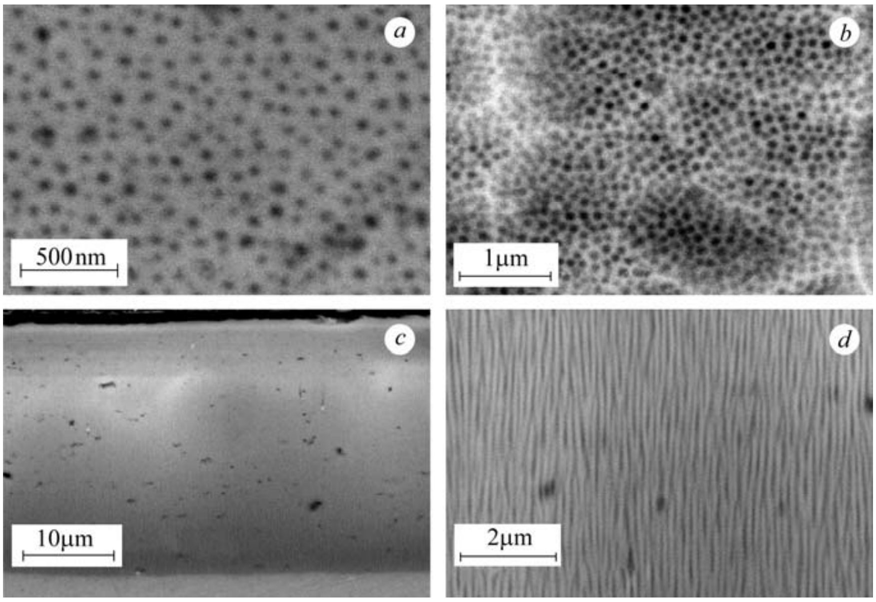

Fig. 2. SEM images of morphology (*a*, *b*) and cross-section (*c*, *d*) of Al_2O_3 oxide layers.

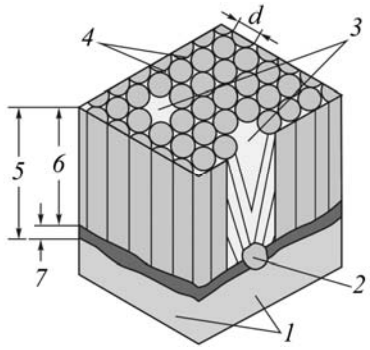

Fig. 3. Model of real structure
of oxide layers of Al_2O_3 obtained via
hard anodic treatment [5]:
1 – metal; *2* – admixture;
3 – microporous; *4* – nanoporous;
5 – oxide cover; *6* – porous layer;
7 – barrier layer.

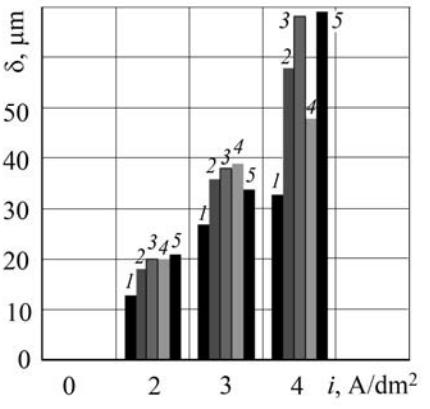

Fig. 4.

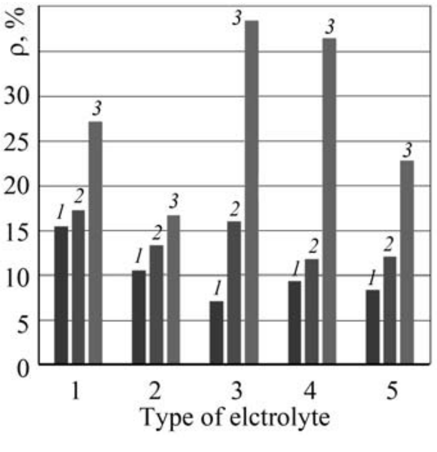

Fig. 5.

Fig. 4. Thickness of the oxide coatings depending on current density in particular electrolytes:
1 – electrolyte 1; *2* – electrolyte 2; *3* – electrolyte 3; *4* – electrolyte 4; *5* – electrolyte 5.

Fig. 5. Volumetric porosity of the oxide coatings depending on the current density in particular electrolytes: *1* – the lowest process parameters; *2* – the medium process parameters;
3 – the highest process parameters.

Based on the tests carried out, characteristics were prepared for the oxide coatings in each of the electrolytes, describing their thickness, porosity and microhardness. Fig. 4 shows the correlations between the thickness of the obtained oxide coatings and current density in the particular electrolytes. Results of porosity measurements of the oxide coatings formed in the particular electrolytes are presented in Fig. 5. A comparative juxtaposition of microhardness measurements of the oxide coatings is shown in Fig. 6.

Changes in the friction coefficient value for the oxide coatings in cooperation with the material applied are presented in Fig. 7.

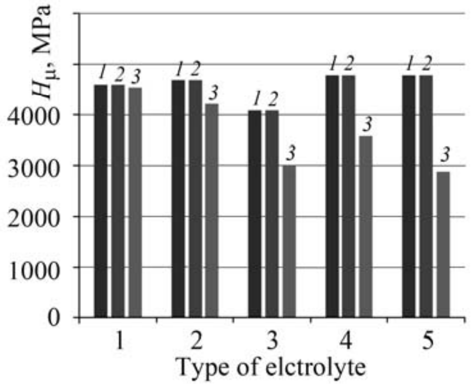

Fig. 6.

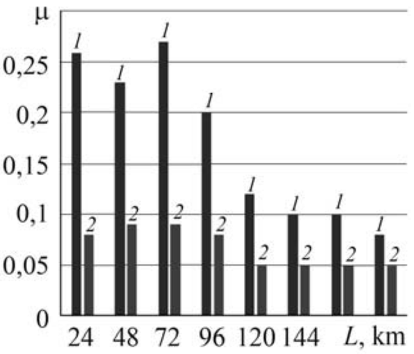

Fig. 7.

Fig. 6. Microhardness of the oxide coatings: *1* – the lowest process parameters; *2* – the medium process parameters; *3* – the highest process parameters.

Fig. 7. Changes in the friction coefficient as a function of friction distance: *1* – specimen with the highest porosity; *2* – specimen with the lowest porosity.

Fig. 8 shows the value of wear intensity of the TGK 20/5 specimens material in their wearing-in period (friction distance: 96 km) and during normal operation.

There are two stages to be distinguished in the period of friction and wear tests of a friction couple: wearing-in; regular operation.

Based on the results obtained, it can be concluded that the friction coefficient of the oxide coating working in a couple with the TGK 20/5 material is significantly affected by the parameters of the oxidation process (current density, electrolyte temperature and oxidation time).

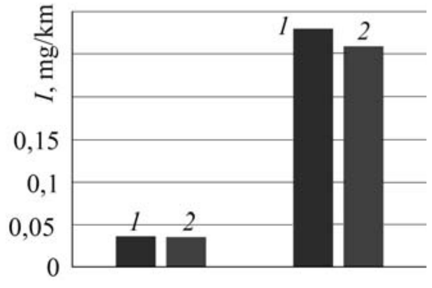

Fig. 8. Intensity of wear of the specimens made from the material in interaction with an oxide coating:
1 – wearing-in;
2 – operation stage.

Measurements of the wear intensity of specimens made from the above-mentioned material under sliding interaction with an oxide coating have shown an 8-fold increase in wear during the wearing-in period and a 7-fold increase at the operation stage in the case of oxide coatings with the highest porosity.

CONCLUSION

From the results of the investigations presented it is possible to obtain oxide coatings with predefined properties by appropriately controlling their production parameters. The microhardness and volumetric porosity of the oxide coatings obtained in three-component electrolytes make these coatings preferred for sliding couples. The addition of organic acid to the electrolyte enables the elimination of the cooling process, which significantly reduces the production cost of the oxide coatings.

Based on the tribological tests it can be affirmed that, compared to other sliding couples which work in the conditions of technically dry friction, the investigated coatings, in particular those obtained with appropriate oxidation parameters, show good tribological properties. Taking into account the wear of the TGK 20/5 material, the tested couple can be applied in lubricant-free compressors or pneumatic servomotors. The cylinder bearing surfaces (in servo-motors) would be strengthened with an oxide coating formed in a three-component electrolyte, and piston rings could be made from TGK 20/5.

РЕЗЮМЕ. Розроблено електроліти для формування нової генерації оксидних покривів на алюмінії. Методом сканівної електронної мікроскопії досліджено вплив органічних додатків до цих електролітів та параметрів анодування алюмінію на наноморфологію та наноструктуру покриву. Застосовано новий покрив у парі ковзання з матеріалом TGK 20/5. Випробувано за умов сухого тертя. Встановлено коефіцієнт тертя пари ковзання, а також інтенсивність зношування зразків з цього матеріалу. Визначено вплив наноструктури оксидного покриву на трибологічні властивості досліджуваної пари.

РЕЗЮМЕ. Разработаны электролиты для формирования новой генерации оксидных покрытий на алюминии. Методом сканирующей электронной микроскопии исследовано влияние органических добавок к этим электролитам и параметров анодирования алюминия на наноморфологию и наноструктуру покрытия. Применено новое покрытие в паре скольжения с материалом TGK 20/5. Испытано в условиях сухого трения. Установлен коэффициент трения пары скольжения, а также интенсивность изнашивания образцов из этого материала. Определено влияние наноструктуры оксидного покрытия на трибологические свойства исследуемой пары.

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