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# SURFACE OXIDE LAYERS WITH AN INCREASED CARBON CONTENT FOR APPLICATIONS IN OIL-LESS TRIBOLOGICAL SYSTEMS

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The paper presents the properties of surface oxide layers with an increased content of carbon for tribological applications. The composite surface oxide layers were produced using a two-step technology through hard anodising of the surface of an aluminium alloy, followed by thermochemical treatment of anodic oxide coatings. The surface oxide layers were subjected to tribological tests in an oil-less sliding couple with T5W plastic. The presented test results confirm the usefulness of the proposed modifications of surface oxide layers for the purpose of enhancing the operational durability of oil-less sliding couples in a reciprocating motion.

**Keywords:** surface oxide layer, composite surface oxide layer, tribology

## 1. INTRODUCTION

Among a number of materials applied in modern fields of technology, aluminium alloys are more and more frequently used as engineering materials. The factors contributing to their wider application (Deuis et al., 1997; Posmyk, 2002) include both very good strength properties coupled with a low specific gravity and low production costs. Electrolytic oxidation of aluminium alloys leads to the formation of an oxide layer  $Al_2O_3$  on their surface. Surface oxide layers, with a thickness from several to a dozen or so micrometers, are characterised by much higher hardness compared to the input material. Owing to such modification, aluminium alloys gain another quality advantageous for engineering materials, namely abrasion resistance (Brace and Sheasby, 1979; Gabe, 2002). Surface oxide layers produced through hard anodising belong to materials with a strongly developed surface and their properties can vary widely, and depend mostly on the conditions in which they are produced. A hard coating of  $Al_2O_3$ , thanks to its very good adhesion to the substrate, high microhardness and adequate thickness to the tribological applications, and low grindability (Brace and Sheasby, 1979; Gabe, 2002; Fratila-Apachitei et al., 2003 a, b) has found applications in oil-less sliding couples with polymers (Wołek and Gołąb, 1995). The improvement of tribological properties of the above-mentioned sliding couples can be obtained through modifications of polymer materials (Friedrich et al., 1995; Takaya et al., 2003) or oxide layers, using metals (Johansson et al., 2003; Posmyk, 2012), polymers (Xingke Zhao and Wenxin Li, 2006; Hui Wang et al., 2005) or solid lubricants (Maejima et al., 2000; Xu Tao et al., 1996) to this end. A modification of surface oxide layers is carried out through immersion, electrolytically, through sputtering, plating, ultrasonically or by means of many other methods which use the techniques of physical and chemical deposition from the gaseous phase (Jiayi Sun et al., 2001; Posmyk, 2002). In the case of coatings applied onto the substrate of aluminium alloys,

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the low temperature of substrate recrystallisation confines the applicability of the above-mentioned modification methods.

The authors of the paper developed new technologies of low-temperature modification of surface oxide layers, whose essence consists in obtaining an increased carbon content in the close-to-surface zone of the coating, thereby leading to a reduction of the friction force in sliding couples with polymers in friction in air (Bara and Skoneczny, 2008; Kmita et al., 2008). Surface oxide layers were produced using a two-step technology through hard anodising of the aluminium alloy surface followed by thermo-chemical treatment of the surface oxide layers. Thermo-chemical treatment of the surface oxide layers was conducted by means of two methods: in graphite dust (Bara et al., 2009) and through sealing in a water solution of succinic acid (Kmita et al., 2008; Kmita and Skoneczny, 2011). This paper presents the operational tests of oil-less pneumatic servo-motors, whose cylinder bearing surfaces were covered with modified surface oxide layers.

## 2. EXPERIMENTAL PROCEDURES

The base material for preparing oxide surface layers were cylinders with an inner diameter of  $\varnothing 3.2 \times 10^{-3}$  m and a length of  $8.7 \times 10^{-3}$  m, made of aluminium alloy EN-AW-6063. The inner surfaces of the cylinder after initial etching in water solutions of KOH and HNO<sub>3</sub> were subjected to hard anodising in a multicomponent electrolyte based on sulphuric acid with an addition of organic acids. The anodising process was carried out at a constant electric charge density of  $106 \text{ A s m}^{-2}$  and a constant temperature of the electrolyte, 303 K. Hard anodising was carried out on a special laboratory stand for the oxidation of pneumatic servo-motor cylinders (Fig. 1). The structure of the stand allowed for the electrolyte to flow in a closed system.

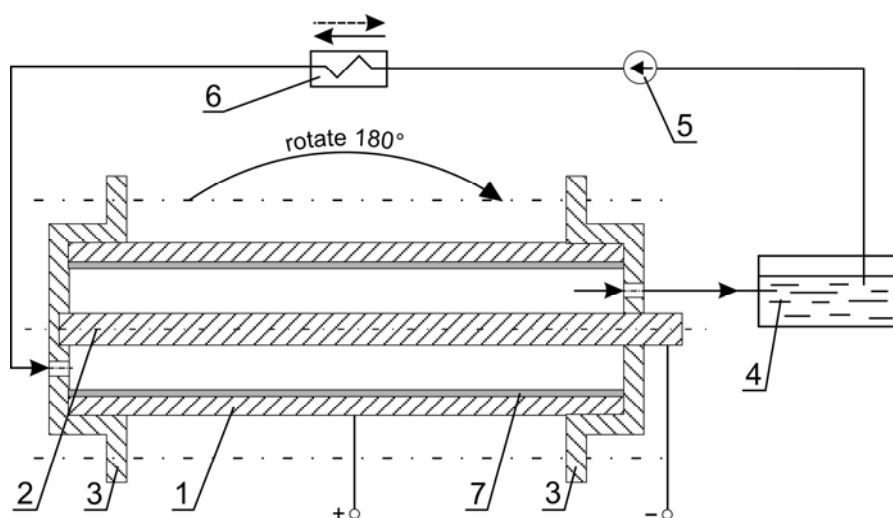


Fig. 1. Diagram of a stand for oxidizing cylinders with forced electrolyte circulation:

- 1-cylinder (anode), 2-cathode, 3-fixing holders, 4-container with electrolyte, 5- pump, 6-heat exchanger, 7-oxide coating

Only the inner surface of the cylinder was subjected to anodising, owing to which it was possible to limit considerably the amount of heat generated in the process of electrolysis. In order to avoid an uneven growth of the surface oxide layers during oxidation, changes were made in the direction of electrolyte flow. To maintain a constant temperature of the electrolyte, a heat exchanger was used in a closed system. The obtained oxide coatings were subjected to thermo-chemical treatment by means of two methods.

The first method of modification consisted of thermo-chemical treatment of the surface oxide layers, which was conducted in a solid medium in the form of graphite dust of 99% purity with a grain size of less than  $2 \times 10^{-6}$  m. The oxidised cylinders, placed in ceramic boxes, were sprinkled with graphite dust and next, soaked in an electric furnace at a temperature of 403 K (threshold temperature of EN-AW-6063 alloy recrystallisation) for  $1.728 \times 10^5$  s. The other modification method consisted of thermo-chemical treatment of the surface oxide layers in organic acids. The thermo-chemical treatment was carried out through sealing the formed coatings of aluminium oxide in a water solution of succinic acid at a temperature of 368 K for  $1.2 \times 10^3$  s.

Tribological tests of the modified layers were repeated three times on a stand used for operational tests of pneumatic servo-motors, which consists of a real pneumatic system with electromagnetic control. A guide ring with a rectangular cross-section, made of T5W material, was a tribological partner in the sliding couple with surface oxide layers (cylinder bearing surfaces). The T5W is a composite material based on PTFE with a dispersion phase in the form of a prepared carbon powder (Fig. 2). An addition of carbon to PTFE results in an increased mechanical resistance, a reduced linear thermal expansion coefficient and reduced abrasive wear.

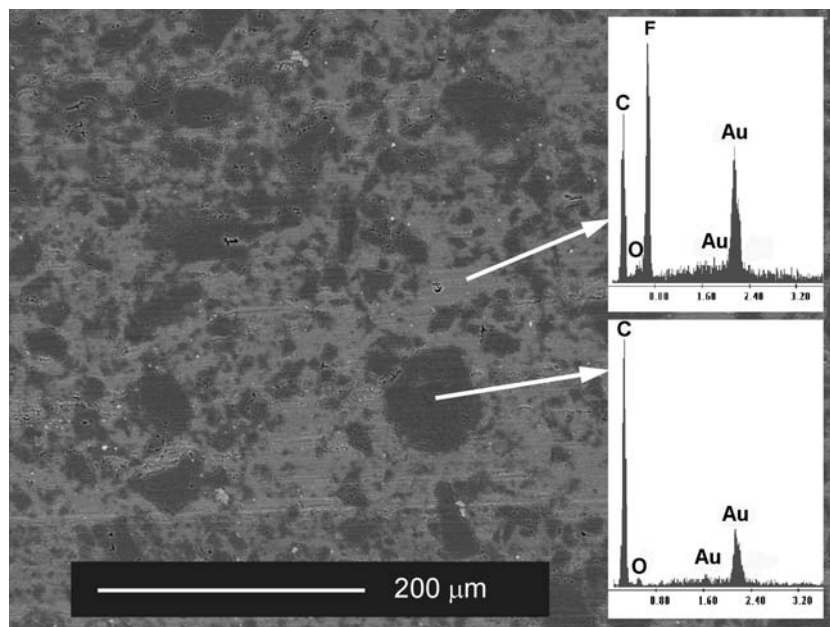


Fig. 2. The SEM image of the surface of the T5W plastic with EDS analysis of the chemical composition

The T5W material, due to its low value of friction coefficient, is applied, among others, in piston-cylinder pneumatic systems. Operational tests of the servo-motors were conducted at a constant speed of  $0.1 \text{ m} \cdot \text{s}^{-1}$  over a distance of  $3.5 \times 10^4$  m. The pressure of the control air supplied to servo-motor chambers was  $0.5 \times 10^6$  Pa. During the test, measurement of the temperature of the servo-motor cylinder was made through placing a K type thermocouple in its central zone. The temperature was measured by means of an analog-to-digital converter SPIDER 8, using the sampling of 1 Hz. Macroscopic images of the cylinders after operational testing were made with a NIKON D40 camera, while images of the structure and morphology of the formed surface oxide layers were made by means of a transmission microscope, JEM 2010 ARP, and scanning microscope, PHILIPS XL30. A gravimetric method was used to measure the intensity of wear of the T5W material, using analytical laboratory scales, WGR60. Roughness of the tested cylinder bearing surfaces was evaluated by means of a contact method, using a profilographometer, FORM TALYSURF SERIES 2. Selected stereometric parameters of the tested surfaces were subjected to an analysis using the Mountains Map Universal programme.

### 3. RESULTS

The tests of the unmodified surface oxide layer structure made by means of a transmission microscope (Fig. 3a) showed a columnar-fibrous structure of the oxide. The aluminium oxide fibres are oriented along the direction of coating growth, arranged in parallel to one another. There are free spaces visible between the oxide fibers, which form a channel for the migration of oxygen ions combining with the anode material during electrolysis. These spaces are free of any dispersion, although, at a high magnification, some inclusions are visible which are the residua of the electrolysis. The image of the unmodified surface oxide layer morphology (Fig. 4a), made by means of scanning electron microscopy, shows surface porosity with nanopores with a cylindrical structure which is characteristic for aluminium oxides. The nanoporosity visible on the entire surface of the layers is the effect of the columnar structure of the oxide layers (Fig. 3a). In the structure of the oxide layer beside nanopores, there are also micro- and mesopores which were formed by dissolution of the dopants of aluminum alloy and energy interference during anodising process. In the picture of the modified oxide layer (Fig. 3b) carbon particles placed in places that make this possible (micro- and mesopores) are to be seen. Carbon precipitates are of a diffusive nature. During the thermo-chemical treatment, graphite dust reacted with oxygen present in the box between powder grains, thereby producing carbon monoxide and dioxide. The formation of carbon dioxide disturbed the balance of the CO–CO<sub>2</sub> mixture, causing absorption of carbon from the environment and formation of CO, until equilibrium was reestablished. Since other CO molecules release atomic carbon at the same time, the reaction proceeded in two directions simultaneously, with the absorption of carbon from the environment and its release in the structure of modified coatings (Bara et al., 2009). Carbon precipitates occur in groups and are composed of small grouped nanometric particles which form bigger agglomerates of micrometric dimensions.

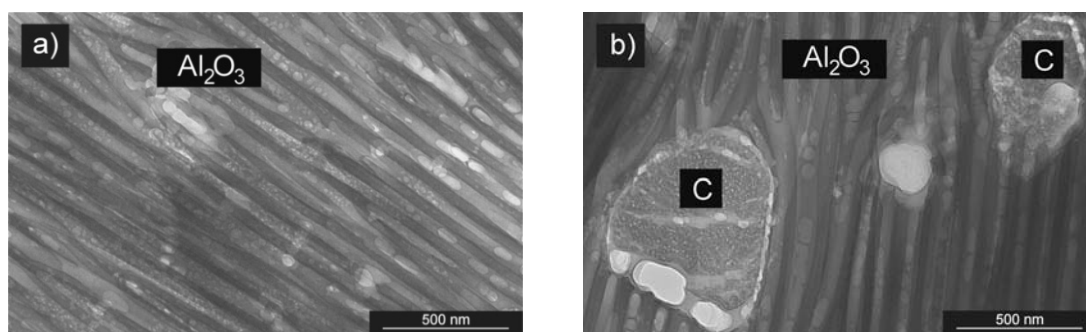


Fig. 3. Image of cross-section of the surface oxide layer a) unmodified, b) modified through thermo-chemical treatment in graphite dust

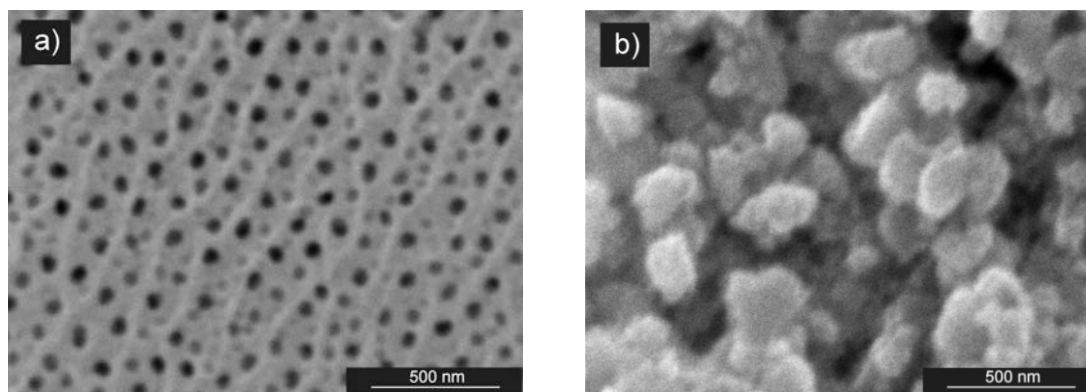


Fig. 4. Image of the oxide layers surface morphology: a) unmodified, b) modified through thermo-chemical treatment in a water solution of succinic acid

The macroscopic image of the surface oxide layer modified through thermo-chemical treatment in a water solution of succinic acid (Fig. 4b) indicates significant or complete sealing up of the oxide coating pores with the products of the applied treatment. The applied thermal treatment of the surface oxide layers led to adsorption of succinic acid in the structure of  $\text{Al}_2\text{O}_3$ , followed by partial decomposition of adsorbed organic compounds (phthalic, oxalic and succinic acids) and creation of new hydrated phases of aluminium oxide. The effects of the above-mentioned process include swelling of aluminium oxide fibres, an increase in the content of carbon compounds in the close-to-surface zone and the sealing up of the porous oxide layers surface with the products of the thermo-chemical treatment applied (Kmita et al., 2008).

Operational tests of surface oxide layers formed on cylinder bearing surfaces showed a significant reduction in the intensity of wear of a piston guide ring interacting with the composite surface oxide layers in relation to the intensity of wear of the guide ring mass in a piston interacting with the surface oxide layers not subjected to modification (Fig. 5). The surface oxide layers modified through thermo-chemical treatment in the graphite dust showed intensity of wear of the guide ring in a servo-motor piston lower by 87% ( $0.015 \times 10^{-6} \text{ g} \cdot \text{m}^{-1}$ ) than in the case of the unmodified surface oxide layers ( $0.113 \times 10^{-6} \text{ g} \cdot \text{m}^{-1}$ ). The surface oxide layers modified through sealing in succinic acid showed a 46% reduction in the intensity of wear of the guide ring of a servo-motor piston ( $0.061 \times 10^{-6} \text{ g} \cdot \text{m}^{-1}$ ) compared to the unmodified surface oxide layers.

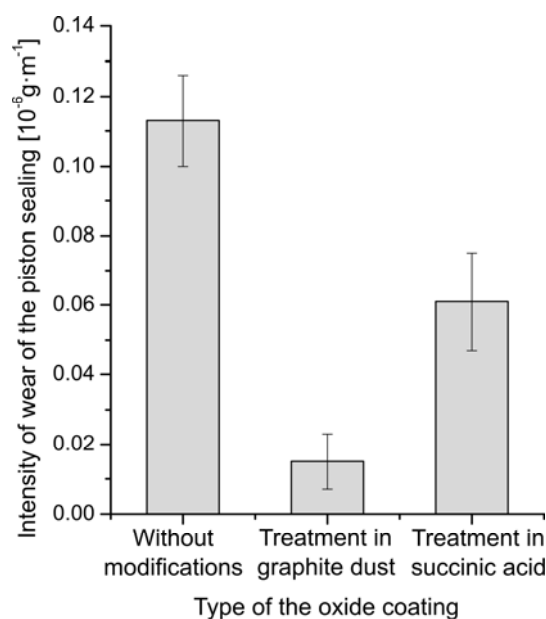


Fig. 5. The intensity of wear of the sealing of a piston interacting with cylinder bearing surfaces unmodified and modified by means of the two-step methods

The reduction in the intensity of wear of the piston guide ring in the sliding couples where the modified cylinder bearing surfaces were applied was also accompanied by a significant reduction in the temperature of the cylinder, recorded during the operational tests (Fig. 6). The reduction in the temperature of the cylinders testifies to a reduction of resistance to motion in the couple consisting of the cylinder bearing surface and the piston guide ring, which resulted from the modifications introduced in the surface oxide layers.

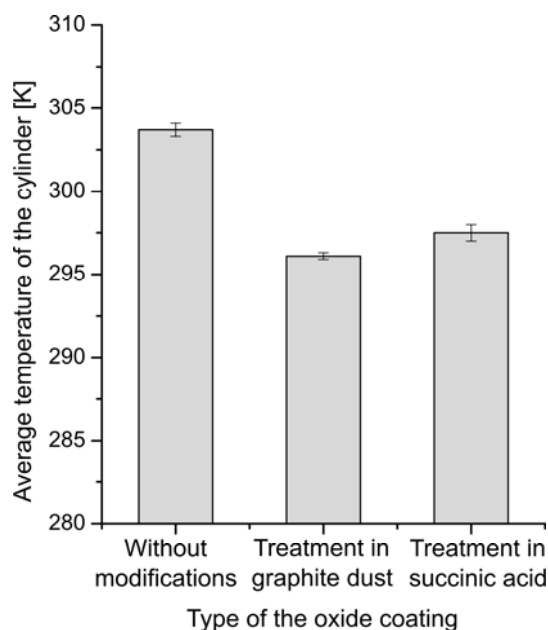


Fig. 6. Mean temperature of a cylinder with a bearing surface: unmodified and modified by means of the two-step methods

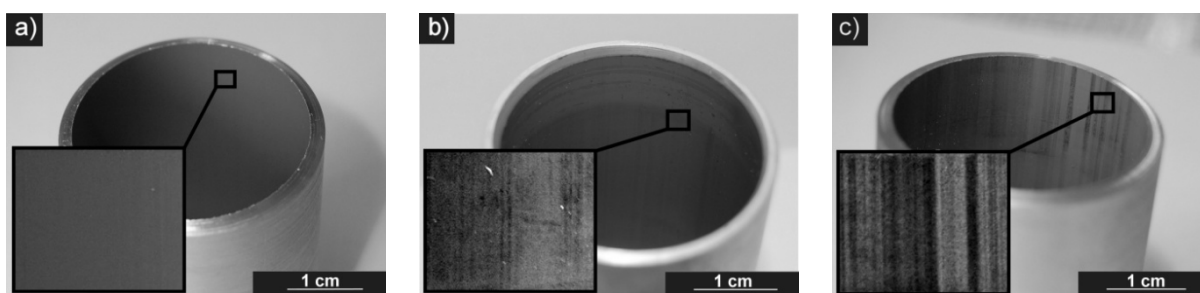


Fig. 7. Images of cylinder bearing surfaces with oxide layers: a) unmodified, b) modified through thermo-chemical treatment in graphite dust, c) modified through thermo-chemical treatment in a water solution of succinic acid

The effect of the interaction in the piston-cylinder sliding couple included the application of a sliding film (Fig. 7b, 7c) onto the cylinder bearing surface whose formation is directly associated with the transfer of the plastic material of the piston guide ring onto the oxide layers surface during the wearing-in process. No presence of a sliding film was observed on the bearing surface of the cylinder with an unmodified surface oxide layers (Fig. 7a). The high value of wear intensity of the piston guide ring interacting with an unmodified surface oxide layers (Fig. 5) can be associated with the predominance of abrasive wear which is characterised by scratching, ploughing or microcutting of the guide ring material. In the case of the surface oxide layers obtained with a two-step technology, the wear of the guide ring was of adhesive nature and caused local tacking of the interacting sliding surfaces, shearing of cohesive bonds within the weaker material and depositing it on a more durable material. This fact is consistent with Bowden's theory.

The results of stereometric tests of coating surfaces (Tab. 1) indicate that the used modifications caused an increase in amplitude parameters of surface roughness ( $S_a 0.35 \times 10^{-6}$  m for non-modified coatings and  $S_a 0.56 \div 0.59 \times 10^{-6}$  m for surface oxide layers subjected to thermal treatment in graphite dust or succinic acid).

Table 1. Stereometric parameters of surface of the surface oxide layers before operational test

Modification of the anodic oxide coating	Stereometric parameters of the surface						
	$Sa$ $10^{-6}$ m	$Sk$ $10^{-6}$ m	$Spk$ $10^{-6}$ m	$Svk$ $10^{-6}$ m	$Sdr$ %	$Sds$ $10^{-6}$ psk·m <sup>-2</sup>	$STp$ %
Anodic oxide coating before modification	0.35	0.72	0.32	0.29	0.357	11908	50.1
Thermal treatment in graphite dust	0.59	1.23	0.38	0.52	0.65	5419	49.6
Thermal treatment in a succinic acid solution	0.56	1.19	0.37	0.56	0.712	9321	52.8

Proportionately higher values were noted also in the analysis of Abbott-Firestone curve parameters ( $Sk$ ,  $Svk$ ,  $Spk$ ). This can be associated with an increased development of oxide layers surfaces subjected to modifications.

This fact is corroborated by the increase of the  $Sdr$  parameter from 35% to 71% in the case of the layers sealed in succinic acid and up to 65% in the case of layers modified through thermo-chemical treatment in graphite dust. This is accompanied by a decrease in the number of peaks of surface irregularities from  $Sds$   $11908 \times 10^{-6}$  psk·m<sup>-2</sup> to  $Sds$   $9321 \times 10^{-6}$  psk·m<sup>-2</sup> (for the layers subjected to thermo-chemical treatment in the succinic acid) and  $Sds$   $5419 \times 10^{-6}$  psk·m<sup>-2</sup> (for the layers modified by the thermo-chemical treatment in the graphite dust). Both the unmodified and modified surface oxide layers showed the nature of a plateaued surface, which is advantageous from the point of view of tribological properties. This is testified by the high values of the surface bearing index,  $STp$  50% for the unmodified layer,  $STp$  49.6% for the coating modified through thermo-chemical treatment in the graphite dust, and  $STp$  52.8% for the layer modified through thermo-chemical treatment in succinic acid.

#### 4. CONCLUSIONS

The presented test results and their interpretation confirm the usefulness of the proposed modifications of surface oxide layers for the purpose of enhancing the operational durability of oil-less sliding couples in a reciprocating motion. The operational tests results show a significant reduction in the intensity of wear of the polymer guide ring of the piston in couples with upper layers produced using the two-step technologies on the bearing surfaces of cylinders in pneumatic servo-motors. It is accompanied by a reduction in the temperature of the cylinders, which testifies to a reduced resistance to motion in the couple. The improvement of tribological properties of surface oxide layers results from the presence of carbon dispersion on the surface and in the structure of coatings formed as a result of the application of thermo-chemical treatment in graphite dust or in a water solution of succinic acid. The products of the thermo-chemical treatment present in the composite oxide coatings allow to change the nature of wear of the sliding couple by facilitating the application of a polymer sliding film. Despite the increase of amplitude parameters of surface roughness in the surface layers, induced by the presence of the thermo-chemical treatment products, the geometric structure of the surface remains beneficial for tribological applications.

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