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TRIBOTECHNICAL CHARACTERISTICS OF FLUORINE-CONTAINING COATINGS

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Abstract: Theoretical and technological bases for the formation of nanophase and nanocomposite fluoroorganic coatings when combining different types of activation effects are presented in the article. On the basis of the carried out studies, developed a technological and practical applications fundamentally new engineering tribological coatings with improved performance characteristics.

Keywords: fluorine-containing oligomers, wear inhibitors, nanoparticles, coatings

1. INTRODUCTION

Analysis of the literature on various aspects of the creation and study of boundary layers, films and coatings, as a section of nanomaterial science, indicates the presence of significant gaps in the theoretical substantiation of the structural features, structure, and physico–chemical parameters of low-dimensional film material objects. The use of classical concepts adopted in solid state physics and molecular and atomic physics, and attempts at their scholastic use to study objects at the interface between atomic (molecular) formations and microobjects with characteristic macrostructure parameters, causes this fact [1–4]. The existence of a large number of experimental, theoretical data in the modern science of nanostate and nanotechnology determines the need to systematize, in a number of cases, inconsistent and fragmented information in order to create scientifically sound ideas about the mechanisms for the formation of surface systems for effective use in solving various engineering problems.

One of the main aspects of nanomaterial science of surface phenomena is the establishment of physicochemical principles for the creation of nanostructured surface layers (films, coatings) and the mechanism of their interaction with the surface of a substance in a condensed state from the point of view of modern concepts of solid state physics, materials science and technology of polymer materials [5–7]. The development of a theoretical framework for solving nanomaterial problems of surface phenomena is based on a systematic approach, including physical, chemical, material science, technological and technical and economic aspects. In connection with the foregoing, the work is devoted to the problem of a complex study of the regularities in the formation of nanostructured thin-film coatings, including the development of physical models for the mechanisms for the formation of the structure of nanocomposite and nanophase films and coatings based on oligomeric and polymer matrices modified by various energy effects, low-dimensional particles of different composition, structure and production technology, and the creation of functional nanostructured coatings with service characteristics, superior analogues specifications wear resistance, resistance to high temperatures, environment, adhesion strength for use in the chemical industry, automotive and special machinery, energy [8–9].

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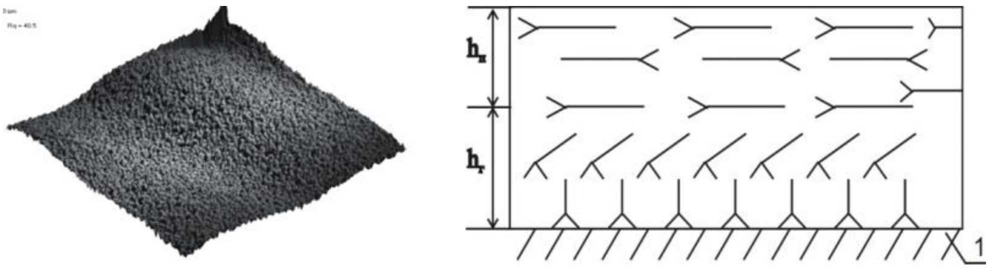
2. EXPERIMENTAL

The following methods and equipment were used during the research. The surface morphology of the samples was investigated by atomic force microscopy (atomic force microscope NT–206 manufactured by ODO "Microtestmashines"). Investigations by IR spectroscopy were carried out using the spectrometer Tensor 27. The microhardness was determined using a PMT–3 device. Tribotechnical characteristics were determined on the FT–2 device (manufacture of ODO "Microtestmashines").

3. RESULTS AND DISCUSSION

The initial steel substrates were ground and polished to 10 surface finish class (Ra=0,16 μm). Thin-film coatings of fluorine-containing oligomers "Foleox" of various compositions are so-called "sandwich structures" consisting of a set of layers of macromolecules with different orientations with respect to the substrate (Fig. 1 a, b). The presence of polar groups (–OH, –COOH, $–NH_2$) in the macromolecule of the oligomer promotes their adsorption interaction with the surface layer of the metal substrate 1 to form a layer with a predominant orientation of the macromolecules perpendicular to the surface plane. The structure of the film combines layers with different ordering due to the weakening of the action of the force field of the surface of the metal substrate. The thickness of the boundary layer and the ratio of the thickness of the ordered and disordered surface layer are determined by the structure of the macromolecule (type and number of polar functional groups) and the activity of the metal substrate (the structure and thickness of the oxide layer, the defectiveness, the charge state, the phase structure, etc.). Such a mechanism for the formation of fluorine-containing coatings, explains the increase in the physico-mechanical characteristics of the materials being processed, and also corresponds to high processability in application.

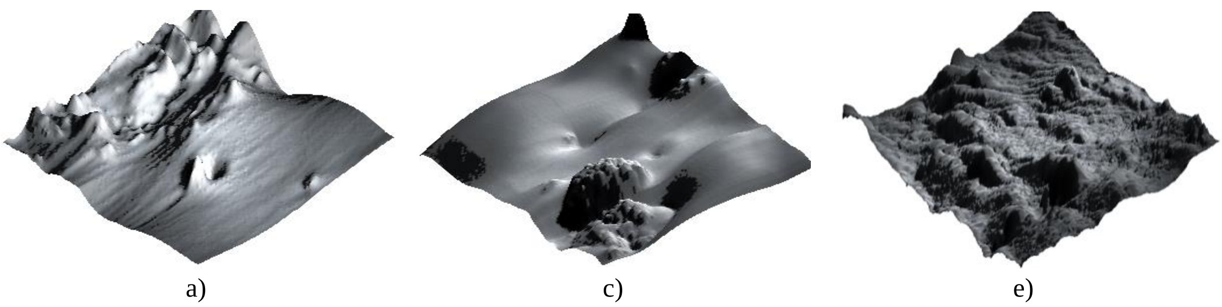


a) b)

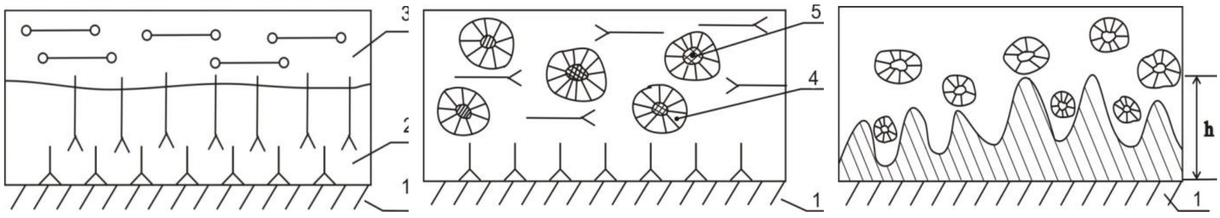
Figure 1. Morphology (a) and scheme of the structure (b) of fluorine-containing oligomers "Foleox" on a substrate of steel C45.

Coatings formed from a combination of polar and non-polar oligomers make it possible to obtain protective layers that combine the high chemical adsorption activity provided by the polar oligomer and the surface layer formed from a nonpolar oligomer with a low shear resistance. These coatings have a high screening effect on the charge surface of a solid.

The use of oligomers of different compositions (polar and nonpolar) allows the formation of a coating combining a chemisorption layer from a polar oligomer with enhanced adhesive strength 2 and a surface layer 3 having a low shear resistance (Fig. 2 a, b).



a) c) e)

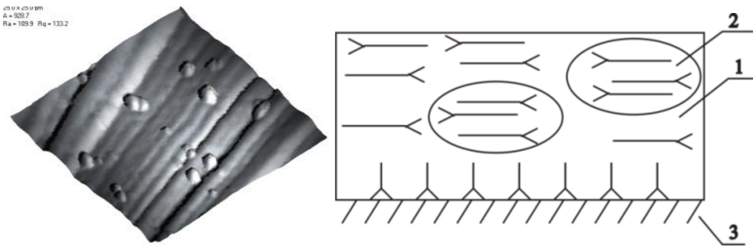


b) d) f)

Figure 2. Morphology (a, c, e) and the structure diagram (b, d, f) of fluorine-containing oligomers "Foleox" on a substrate of steel C45 of two-layer (a, b), filled with nanoparticles (c, d), with a sublayer of titanium nitride (e, f).

Heat treatment of polar fluorine-containing oligomers on different metal substrates leads to similar results. The effect of temperature on the nonpolar fluorine-containing oligomer causes crystal formation processes, only the crystal structure is 4 to 5 times smaller in size than the crystals formed in the coating formed from the polar folate. The increase in specific surface values in FCO coatings during heat treatment is established.

Structural changes occurring in coatings of fluorine-containing oligomers during heat treatment are caused by a decrease in the surface energy values as a result of recrystallization of the ionic processes leading to the formation of quasicrystalline particles having different dispersity, including those located in the nano–region. It is possible to propose the following model of the influence of heat treatment on the structure of fluorine-containing coatings. Heat treatment has a structuring effect on the coating formed on solids, which determines the formation of a quasicrystalline nanophase, the content of which is determined by technological processing parameters (temperature, time). With increasing values of the temperature effect, a nanophase coating with a characteristic structure consisting of an oligomeric matrix (1) and reinforcing phases (2) is formed (Fig. 3 a, b).

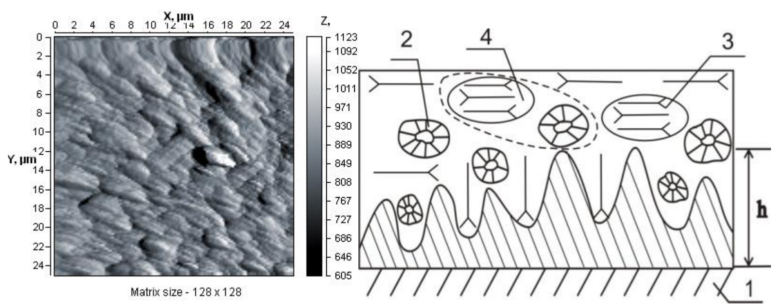


a) b)

Figure 3. Morphology (a) and scheme of structure (b) of coatings of fluorine-containing oligomers "Foleox" on a substrate of steel C45 heat-treated at 523 K.

Proceeding from the obtained data, it follows that during the heat treatment of fluorine-containing coatings formed on active sublayers (titanium nitride, electrolytic chromium modified by particles of ultradispersed diamond), a complex mechanism for modifying the oligomeric matrix of fluorine-containing compounds is realized: the formation of a quasicrystalline nanophase and the structuring of the matrix by low-dimensional particles having an uncompensated charge.

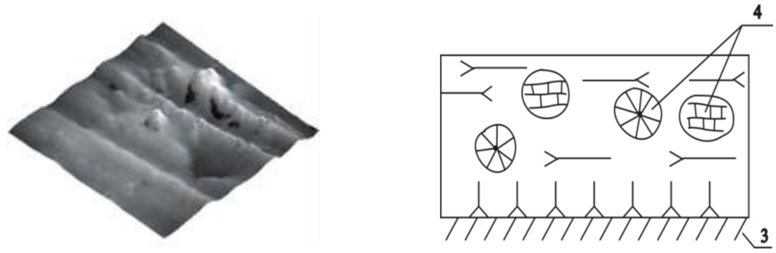
Agglomerated particles (4) are formed, consisting of structured regions (2) and quasicrystalline nanophase (3) (Fig. 4).



a) b)

Figure 4. Morphology (a) and scheme of the structure (b) of a coating of fluorine-containing oligomers "Foleox" on a substrate of titanium nitride containing a drop phase and heat-treated at 473 K.

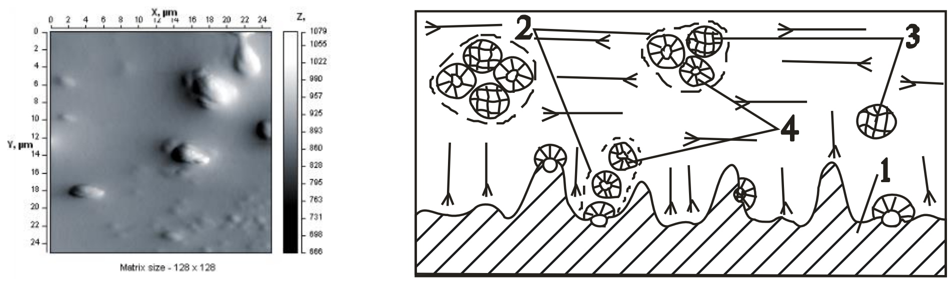
The influence of technological factors on fluorine-containing coatings (for example, soft X-ray radiation) causes a structuring effect on the mechanism of formation in the volume of the reinforcing phases formed as a result of radical transformations. The structure of fluorine-containing layers formed on a solid surface (3), in this case, includes supramolecular and structured phases (4), reinforcing the coating and increasing its physico-mechanical characteristics (Fig. 5 a, b).



a) b)

Figure 5. Morphology (a) and scheme of structure (b) of coatings of fluorine-containing oligomers "Foleox" on a substrate of steel C45, processed by X-rays.

The use of a joint energy action and the modification by low-dimensional particles of a polymer-oligomeric matrix of the fluorine-containing coating results in a synergistic effect of the transformation of the film structure. With this processing, nanostructured agglomerates (2) are formed in the coating structure consisting of clusters (Fig. 6 a, b) obtained by modification with nanodispersed particles (4) and under the influence of external energy parameters (3) (heat treatment, exposure to ionizing and laser radiation, electric and other fields). The resulting quasicrystalline objects in terms of their geometric parameters exceed the thickness of the FCO film, which affects their morphology.



a) b)

Figure 6. Morphology (a) and scheme of structure (b) of coatings of fluorine-containing oligomers "Foleox" on a substrate of steel C45, irradiated with soft x-rays (30 minutes) and filled with nanoparticles.

It is established that treatment with fluorine-containing oligomers of metal substrates leads to an increase in strength characteristics (Fig. 7).

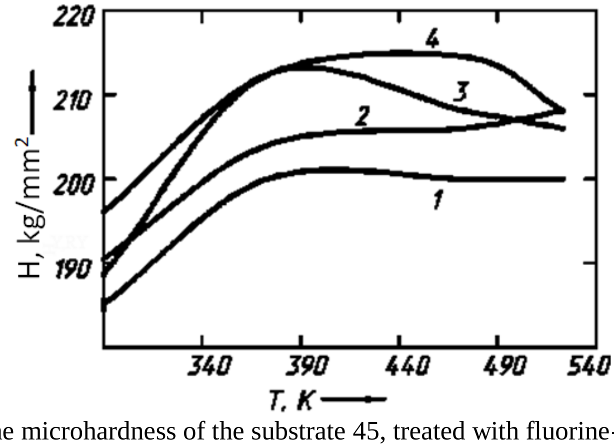


Figure 7. Dependence of the microhardness of the substrate 45, treated with fluorine-containing oligomers, on the heat treatment regime: 1 – steel C45 (initial), 2 – steel C45 + B1, 3 – steel C45 + FAK-2, 4 – steel C45 + F14.

This effect is explained by the process of chemisorption of polar molecules on a metal substrate, as a result of which microdefects are healed in the surface layers of polycrystals, the free energy of surface layers of metal increases, which makes dislocation exit to the surface more difficult. The chemisorption of the molecules of the "Foleox" is confirmed by IR-spectroscopy, the hardware methods of which indicate the appearance of absorption bands in the 1610–1690 cm^{-1} region, which are identified as the absorption bands belonging to metal salts $(COO)_2Me$. This effect depends both on the brand of the fluorine-containing oligomer used, and the type of energy impact and its duration.

The use of fluorine-containing oligomers to create antifriction layers of isolation, especially in friction in the absence or lack of lubrication, when it is not possible to completely separate the contacting surfaces. The study of the influence of loading regimes and the type of lubricant on the coefficient of friction of the model pair "metal-metal" leads to the following results: application of polar fluorine-containing oligomers (F1 type), an average of 3 times and the values of the function f (P) decrease with increasing load. The introduction of a liquid lubricant into low friction zone. Thus, the use of polar fluorine-containing oligomers is the most effective at low sliding speeds of metal friction surfaces operating without lubrication, i.e. at the "start-stop" modes, when V = 0, and the liquid lubricant has practically no effect on the frictional characteristics of the friction unit.

The action mechanism of fluorine-containing high-molecular components of thin-film coatings with using of various techniques (solution, rotaprint, vacuum, mechanochemical) has plenty going for the common control methods of energy and morphological parameters of metal-polymer system elements, becauseit provides highly efficient of inhibitory effect on the wear process, does not require using of special machine-tool attachments (sand wheel blasting, phosphatization, etc.) and can be used in precision friction units. The presence of fluorine-containing high-molecular compounds sublayer helps to reduce the running-in time of friction unit and to the formation of separation (transferred) layer with a specific surface area W = 0,85 ÷ 0,95 of the total area of friction surface (Fig. 8). Thus, taking the energy and morphological factors into account for choosing of the composition and components application technology, which provide the inhibitor effect of the metal-polymer tribological system wear process, determines attainment of the service life and reliability high parameters.

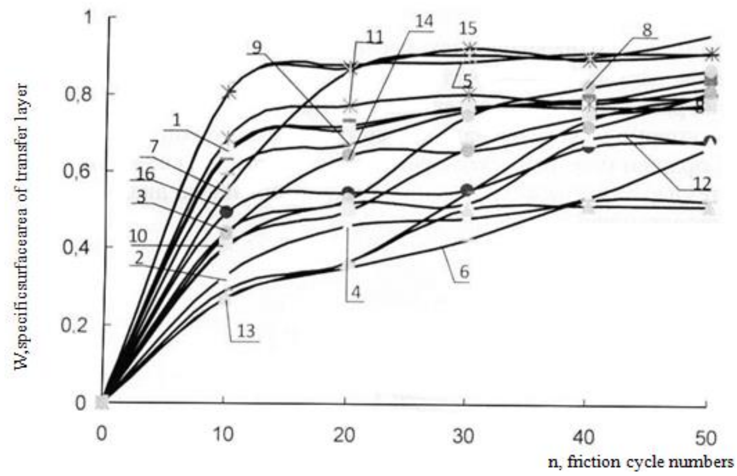


Figure 8. The kinetics of mass transfer for friction process of the carbon sample with various surface pre-treatment counterbody: 1 – TiN + F-1; 2 – phosphate layer (5 min) + F-14; 3 – phosphate layer (15 min) + F-1; 4 – TiN + F-14; 5 – TiN (dropping phase) + F-1; 6 – phosphate layer (15 min) + F-14; 7 – steel C45 + sandblasting + F-1; 8 – steel C45 + sandblasting + F-14; 9 –TiN (droppping phase) + F-14; 10 – phosphate layer (30 min) + F-14; 11 – phosphate layer (30 min) + F-1; 12 –steel C45 + F-14; 13 –steel C45 + F-1; 14 – phosphate layer (5 min) + F-1 + F-14; 15 – phosphate layer (5 min) + F-1; 16 – TiN + F-1+ F-14.

4. CONCLUSION

A phenomenological model for the formation of thin-layer coatings from solutions of fluorine-containing oligomers on substrates of various nature has been developed. The validity of this model in the considered temperature range and radiation doses has been experimentally confirmed. The proposed model of the frictional interaction of a polymer-metal friction pair, including when operating in the field of action of ionizing radiation, is in satisfactory agreement with practical results.

Tribological characteristics of thin-film coatings based on fluorine-containing oligomers "Foleox" at friction nodes under forward and reverse motion are investigated. It is established that the greatest effect in reducing the coefficient of friction and wear intensity of the "Foleox" film is provided when the unit is operated in the "start - stop" and reverse mode. Polar oligomers form adhesively strong tribotechnical films. It is established that technological aspects are of decisive importance in the formation of thin-film coatings from oligomers "Foleox" on the tribotechnical characteristics of metal-polymer tribosystems. The tribotechnical characteristics of coatings formed from fluorine-containing oligomers on heterophase substrates were investigated. The main mechanism for explaining the effect of polymer fluorine-containing coatings formed from the solution is the formation of a chemisorbed or adherently bonded film with a substrate with a low wear resistance preventing the setting on the spots of the actual contact "modified intermetallide-metal", "modified metal-metal", "modified metallic compound-metal". The complex application of nanodispersed particles and coatings formed from fluorine-containing oligomers made it possible to obtain a synergistic effect, manifested in a sharp decrease in the friction coefficient and wear rate while simultaneously increasing the corrosion resistance of the modified substrates. Energy state of the metal component of surface layer of the metal-polymer tribological system characterized by the presence of a charge mosaic determines necessity for the using of special components for the formation of the separation layer with high stability. As components for the formation of wear inhibitors are effective the fluorine-containing polymer and oligomer compounds coated by solution, rotaprint or vacuum techniques.

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