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Physical and chemical processes in the application of antifriction coatings by the friction-mechanical method

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Abstract

A review of current models of antifriction coating formation by finishing antifriction non-abrasive treatment has shown the lack of a thorough analysis of physical and chemical processes occurring in the friction zone. From this point of view, it seems reasonable to study the process of coating formation at the stages of surface activation, deposition of antifriction components and formation of an antifriction coating. The considered characteristic structures for each of the stages of antifriction coating application and chemical reactions that occur during the formation of an antifriction coating allow us to track the processes accompanying the formation of coatings and identify ways to improve them. It is proved that the quality of coating formation directly depends on the material of the part and tool, temperature in the deposition zone, material diffusion rate, and dissociation of chemical compounds. A physical model of the process of finishing antifriction non-abrasive treatment is proposed, which determines the chemical reactions and physical processes occurring at different stages of the antifriction coating formation. The analysis of the model allows to find out and explain the characteristic phenomena in the system 'part – tool – technological environment', and, therefore, to influence the quality of the formation of an antifriction coating by the friction-mechanical method.

Key words: finishing antifriction non-abrasive treatment, physical model, antifriction coating, process medium, surface activation, tribodestruction, wear resistance

Introduction

Methods of hardening treatment and modification of working surfaces to improve the performance of friction surfaces are becoming increasingly common. The development of these methods is primarily driven by the growing demands on the durability and performance of machine parts. Wear resistance, bearing capacity, fatigue and contact strength are determined by the initial physical and mechanical state of the contacting surfaces (surface layers), and protective coatings must provide the required tribotechnical properties in a wide range under various operating conditions [1]. It should be noted that for each specific friction pair they may differ.

One of the most promising methods of applying wear-resistant coatings is the finishing antifriction non-abrasive treatment (FANT) of parts [2]. The essence of the method is that the parts are coated with thin layers of soft metals such as copper, brass, and bronze using friction [3]. Currently, there are several technological variants of FANT. In the friction-mechanical method, the antifriction coating is applied to the part by pressing a brass or copper bar in a glycerine medium and transferring the bar particles to the surface of the part. The pressing force reaches 20...70 MPa, the process is accompanied by significant heat generation, and the thickness of the applied coating is in the range of 2 to 10 μm [4].

There are other technological variants of FANT, in which the coating is applied in a liquid medium containing inorganic copper compounds and surfactants [5]. In this case, the metal coating is obtained as a result of physical and chemical processes that occur between the working medium and the workpiece during mechanical activation of the surface by the tool. The tool can be made of various materials, such as rubber, polyurethane, felt, etc.

Despite the simple kinematics and the nature of the tool-surface interaction, the FANT process is based on force and thermal effects, accompanied by a whole range of rather complex thermal, deformation, tribophysical and chemical processes.

The development of scientific foundations for increasing the durability of machine parts subjected to hardening treatment with coating by FANT methods within the framework of an integrated approach is impossible without establishing and describing the whole variety of physical phenomena accompanying this process and the parameters that determine the quality of the surface and surface layer, which determine the level of operational properties.

There are various hypotheses explaining the mechanism of coating formation in FANT. These mechanisms are described in scientific sources of information. However, due to the lack of consensus on this issue, as well as in order to improve the authors' coating technology using FANT methods, the coating formation process requires further more detailed study.

Therefore, this work is devoted to the study of physical phenomena and chemical processes occurring during the application of wear-resistant coatings by FANT methods.

Literature review

According to research [6], the formation of antifriction coatings by the FANT method is carried out in eleven stages. The author states that at the first stage, the adhesive zone is formed due to the forceful impact of the tool on the workpiece. At the second stage, the process of dispersion of irregularities and opening of juvenile surfaces takes place. The third stage is characterised by the transfer of iron atoms from the workpiece to the process medium. At the fourth stage, a chemical substitution reaction takes place on the unoxidised surface areas and more active metal ions from the process medium are deposited on the iron surface of the part. The fifth stage is caused by the chemical reactions that form pure metal compounds on the surface from individual ions. The sixth stage is the formation of a protective coating on the surface of the part from particles of dispersed metal from the process medium. The seventh stage is due to the presence in the process medium of individual wear products covered with oxide films, which also participate in the formation of the coating, packing into the overall structure of the coating, they cause the eighth stage. The ninth stage is the diffusion of the coating metal deep into the part. The tenth stage is the prevention of dislocations from reaching the surface of the part. The eleventh stage is deformation of the resulting protective coating.

In our opinion, this model is rather complicated in terms of its further development and improvement, and also does not fully take into account the chemical interaction of the components of the ‘part-tool-technological environment’ system.

In [7], the process of FANT is considered as three separate stages:

- surface pretreatment to strengthen and activate the surface of the base metal, obtaining a juvenile surface;
- chemical interaction of the coating components (the process of restoring the coating metal from the salts of the process fluid) formation of the diffusion layer (dislocation and grain boundary diffusion);
- coating layer growth, interaction of damping tool with the coating, strengthening of the coating and substrate.

In [8], the process of frictional material transfer is divided into two stages:

- plastic squeezing of the initial material, carried out by micro-indentations of the body on which the coating is applied, which proceeds to destruction by micro-cutting;
- adhesion of the chips formed as a result of microcutting to the surface to which the metal is transferred.

In [9], the FANT process is described in three stages. At the first stage, a surface-active medium is applied to the surface of the part, which, having good wetting properties, helps to soften and dissolve oxide films on the surface of the part. The second stage involves the contact of the workpiece with a soft counter body (tool). This stage describes the processes of tool wear due to micro-cutting by irregularities in the workpiece surface. The third stage involves increasing the thickness of the coating as a result of the adhesive forces between the coating material and the workpiece.

In our opinion, this model does not sufficiently take into account the chemical processes that occur as a result of the interaction of the components of the technological environment, as well as the tool and the workpiece.

Paper [10] describes the process of copper-containing coating formation using a gallium-indium process medium. It is shown that due to the kinematic (rotational movement) deformation load of the contact zones, chemical and thermal effects of the gallium-indium component, it is possible to carry out the process of selective dissolution of the copper alloy with the formation of a plasticised copper film on both friction surfaces. Such a structure is considered as a multicomponent - a copper frame with alloying elements of materials adsorbed on the surface, which interact.

In [11], the authors proposed a theoretical scheme of the FABO process carried out by the friction-mechanical method (Fig. 1).

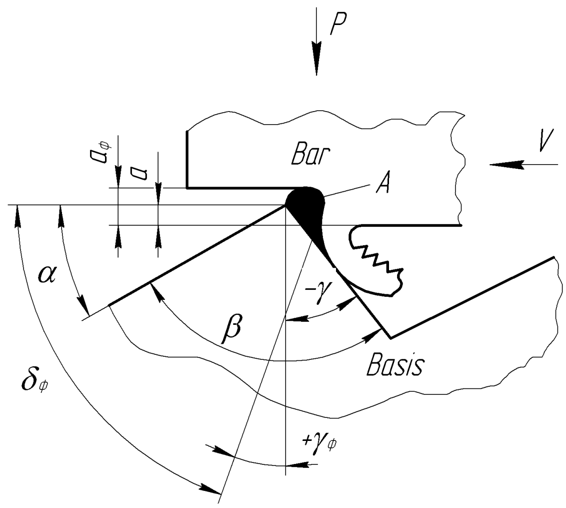

Fig. 1. The theoretical scheme of the process of microcutting during the formation of an anti-friction coating by the friction-mechanical method: *P* – force; *V* – displacement; *a, a*$_Ф$ – theoretical and actual thickness of the cut layer; α, β, γ, δ – cutting angles [11]

The authors argue that at the initial stage of coating formation, the process of micro-cutting takes place. The paper discusses the features of filling the depressions of the microrelief of a part with an antifriction material. The coating process is divided into the following stages:

- mechanical surface preparation with the formation of a regular microrelief;
- coating application using a friction-mechanical method;
- deforming drawing.

However, this approach to considering FANT also does not fully take into account the chemical processes that occur during the formation of an antifriction coating.

Purpose

The aim of the work is to form modern ideas about the processes occurring during the application of antifriction coatings by finishing antifriction non-abrasive treatment.

Results

In our opinion, for an objective assessment of the processes occurring during the application of antifriction coatings, it is necessary to consider the initial state of the surface, as well as the physical and chemical phenomena occurring during the creation of antifriction coatings. From this point of view, it is advisable to analyse the FANT process at the stages of surface activation, deposition of antifriction components and formation of the antifriction coating.

Surface condition before FANT antifriction coating application. It should be noted that the original surface of the part before applying FANT antifriction coatings is characterised by structures that can prevent direct contact and adhesive bonding of metals during the application of the antifriction coating. In addition to moisture in the surface layer, oxides are created on the surface layer as a result of the interaction of air oxygen and the metal of the part (FeO, Fe_2O_3, Fe_3O_4) , as well as chemically absorbed oxygen (Fig. 2).

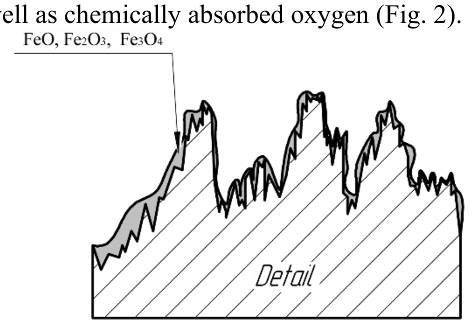

Fig. 2. Initial condition of the surface of the part before applying the antifriction coating

Activation of workpiece and tool surfaces. This stage of coating formation is characterised by the dispersion of the materials of the friction pair - tool and workpiece.

The triggering of the mechanical activation factor during friction coating occurs as a result of frictional interaction, which can partially or completely destroy the oxide layer or chemically absorbed oxygen. The brittle oxide layer on the friction surface is subjected to significant shear deformation, which results in the destruction of the part and tool materials and removal from the contact zone.

The tops of the tool and workpiece micro-exposures are destroyed and the material is removed into the process medium. At this stage, a short-term exposure of juvenile surfaces is possible due to the presence of friction forces between the unevenness of the tool and workpiece surfaces. The activation of the contact surfaces of the workpiece and the tool promotes the formation of interatomic bonds between the coating and workpiece materials.

The duration of the atoms in the activated state is quite short, and therefore the re-formation of metal-oxygen bonds is possible. This is prevented by the surface-active components of the process medium.

This stage is characterised by high pressure on the metal surfaces of the workpiece and tool, as well as local temperature increases in the contact zone of uneven surfaces.

The tool's clamping force and the speed of its movement along the workpiece surface, as well as its own movements (rotation, oscillation, oscillation, impact, etc.) determine the value of the specific heat of friction and, consequently, the contact temperature.

As a result of the mechanical interaction of the soft tool material with the harder workpiece material, a layer of the tool material is removed due to the micro-cutting processes of the workpiece surface protrusions. This stage is characterised by high pressures and the associated penetration of the protrusions of the workpiece surface irregularities into the surface of the softer material that forms the coating.

An increase in temperature in local contact surfaces promotes the excitation of surface metal atoms involved in frictional interaction, which facilitates the destruction of metal-oxygen bonds and provides a temperature factor for the activation of the FANT process.

In this case, it is advisable to use the hypothesis of the coating formation process that occurs as a result of the transition through the activation barrier [1]. A diagram illustrating this theory is shown in Fig. 3. When the activation energy reaches a certain value (the value is determined by the chemical composition of the base material), conditions are created for the destruction of surface oxide films, which ensures the beginning of the process of chemical interaction of the process medium components with the part.

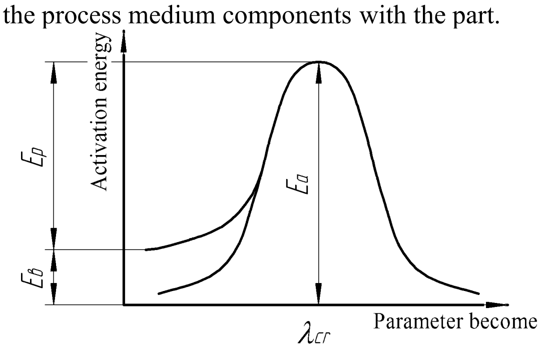

Fig. 3. Energy change during chemical interaction of the coating material and the substrate: λ_{cr} – is the parameter at which the instability of the system occurs; E_a – is the activation energy of the transition to the active state of the system; E_p – is the energy of mechanical action; $E_в$ – is the energy of overcoming the energy barrier [1]

Under such conditions, complex chemical transformations occur in the technological environment, which is based on glycerol [12].

As a result of the interaction of the components of technological media, glycerol tribodestruction occurs, a condition for which is the provision of local temperatures in the friction zone of about 180...280 °C, which are achieved by heat generation in the friction zone of the tool and part.

Tribodestruction is the process of destruction of glycerol ($C_3H_8O_3$) molecules when it interacts with the contacting surfaces of the part-tool system to produce glycerol aldehyde ($C_3H_6O_3$), formaldehyde (CH_2O) and acrolein C_3H_4O. The scheme of glycerol tribodegradation will be as follows:

$$C_3H_8O_3 \rightarrow CH_2O + C_3H_6O_3 + C_3H_4O \qquad (1)$$

These oxidation products, in turn, actively interact with the surface of the part. They contribute to the further formation of a copper film on the surface of the steel part, which reduces the friction coefficient, increases oil capacity and wear resistance, and also participates in the restoration of metal components.

In the process medium used for FANT, one of the main components containing the cladding element is copper chloride $CuCl_2$. Copper chloride in the process medium solution dissociates with the subsequent formation of copper oxide CuO and interacts with other components of the medium.

The dissociation equation for copper chloride is:

$$CuCl_2 \cdot 2H_2O \rightarrow 2HCl_2 + CuO + H_2\uparrow \qquad (2)$$

Also, at this stage, there is a chemical interaction between the surfactants present in the medium and the metal ions present.

Stearic acid is most often used as a surface active agent in the FANT of machine parts ($C_{17}H_{35}COOH$), belonging to organic fatty acids and performing the following functions: destruction of oxide films, plasticisation of surfaces, and reduction of surface tension of the process medium liquid.

The destruction of oxide films on the surfaces of parts and tools contributes to the exposure of the active juvenile metal surface of the part and tool with the subsequent formation of protective coatings from compounds formed by these metals. This is confirmed by the following works [12].

Stearic acid ($C_{17}H_{35}COOH$) reacts with the metal of the workpiece surface (Fe), and with the copper (Cu) of the process medium, thus having a positive effect on the destruction of the oxide film, while stearic acid forms complex compounds with the copper of the process medium and the iron of the workpiece, with the following reactions occurring:

$$2C_{17}H_{35}COOH+Cu^{2+}\rightarrow(C_{17}H_{35}COO)_2Cu+2H^{+}; \quad (3)$$

$$2C_{17}H_{35}COOH+Fe^{2+}\rightarrow(C_{17}H_{35}COO)_2Fe+2H^{+}. \quad (4)$$

As a result of reactions (3) and (4), the compounds $(C_{17}H_{35}COO)_2Cu$ – copper stearate and $(C_{17}H_{35}COO)_2Fe$ – iron stearate are formed. When they get into the microrelief of the part, the following complex compounds increase the resistance to surface wear.

The above chemical reactions and physical processes occurring at the first stage can be represented in the form of a scheme (Fig. 4).

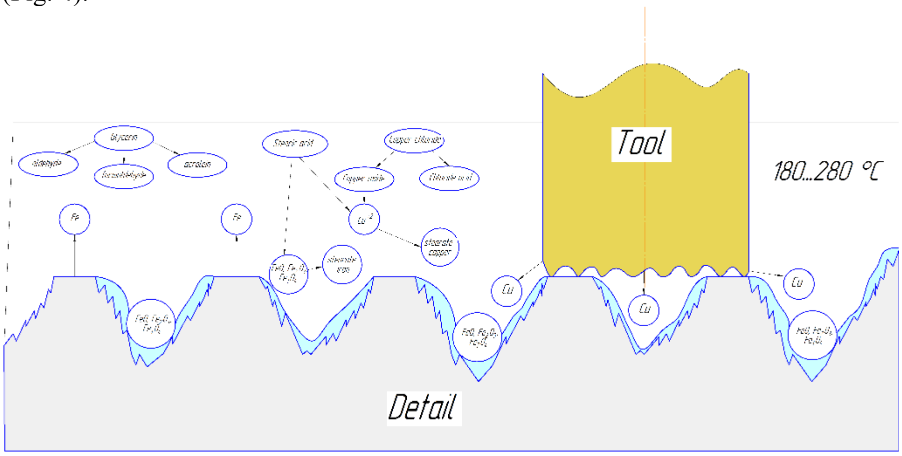

Fig. 4. Scheme of the activation stage of workpiece and tool surfaces

Deposition of anti-friction components on the surface of the part. At this stage, the process of chemical precipitation of metals from copper oxide formed from a chemical reaction (2) takes place.

As a result of tribological loads and pressures, some of the tool material particles formed as a result of cutting are pressed into the depressions between the protrusions of the part's surface profile. This results in surface smoothing, an increase in the actual contact area, and a reduction in contact pressure when the part is working with an antifriction coating. As a result of high local pressures, cohesive bonds are formed between individual particles of the coating material.

In the process medium, formaldehyde CH_2O and acrolein C_3H_4O, as products of reaction (1) of the thermal decomposition of glycerol, react with copper oxide with subsequent reduction of copper Cu on the surface of the workpiece:

$$CH_2O+CuO\rightarrow HCOOH+Cu; \quad (5)$$

$$C_3H_4O+CuO\rightarrow C_3H_6O_4+Cu. \quad (6)$$

As a result, more active copper ions contained in the process medium are deposited on the bare juvenile surface of the part.

The glyceric acid $C_3H_6O_4$ formed during reaction (6) interacts with the part material (Fe), improving the mechanical and tribotechnical characteristics of the applied coating, which is an important aspect for ensuring high wear resistance and long-term operation of the part under increased loads [12].

The reaction of the interaction of glyceric acid with the material of the part will be as follows:

$$\mathrm{Fe^{+2}+C_3H_6O_4\rightarrow[C_3H_6O_4]}. \quad (7)$$

The reaction (7) results in the formation of the complex compound $[C_3H_6O_4]_2Fe$, an iron glycerate that is involved in the formation of the coating.

In addition to copper ions from the process medium, particles of the workpiece material that were separated in the first stage are involved in the formation of the coating. These particles are coated with thin layers of antifriction material due to chemical interaction with the process medium, forming a clad material that is also deposited on the surface of the part.

The chemical reactions and physical processes that take place at this stage can be represented as follows (Fig. 5).

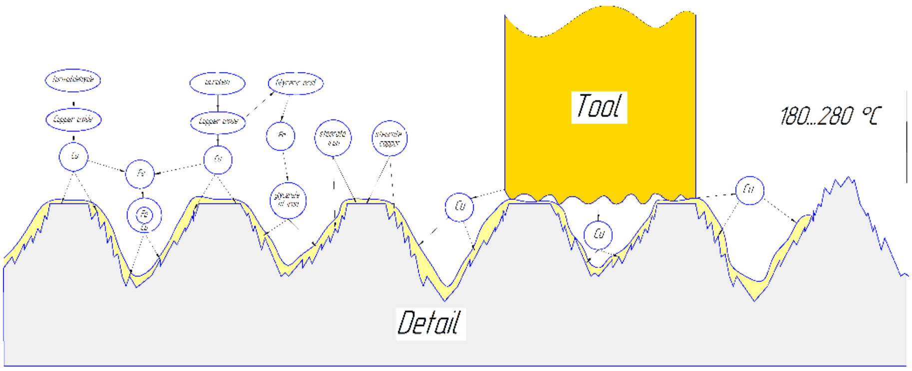

Fig. 5. Scheme of the processes that take place at the stage of deposition of antifriction components on the surface of the part

The processes discussed above suggest that the formation of a coating depends on the material of the part, the temperature in the deposition zone, the interaction time, the rate of diffusion into the material, and the dissociation of chemical compounds.

The concentration of metal salts plays an important role in the course of chemical reactions.

Thus, the concentration of copper in the process fluid, according to [7], increases with increasing acidity *pH* (Fig. 6).

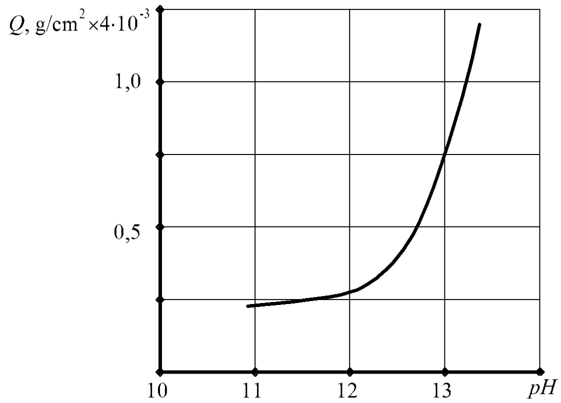

Fig. 6. Dependence of the coating deposition rate on the acidity of the *pH* of the medium [7]

Copper reduction begins at an acidity greater than 11, and the deposition rate increases with increasing acidity. The *pH* value for concentrated solutions can be as high as 11.5. Complexing agents, such as amino acetic acids and glycerol, included in the process fluid, not only increase the solubility of copper salts, but also affect the process of copper ion reduction on the deposition surface.

Reliable adhesion of the coating to the substrate can only be achieved if the coating material diffuses into the base metal.

The formation of a high-quality antifriction coating is ensured by sufficient adhesion and is due to a reduction in the surface roughness of the part and an increase in the total contact area due to the filling of the base metal surface depressions with the coating material. Applying an antifriction coating to a part reduces the friction forces that occur during its operation, thereby reducing its stress-strain state.

Formation of an anti-friction coating. At this stage, the transfer of tool material to the surface of the workpiece is completed (Fig. 7). The coating build-up stops as the equilibrium state is reached in terms of shear characteristics.

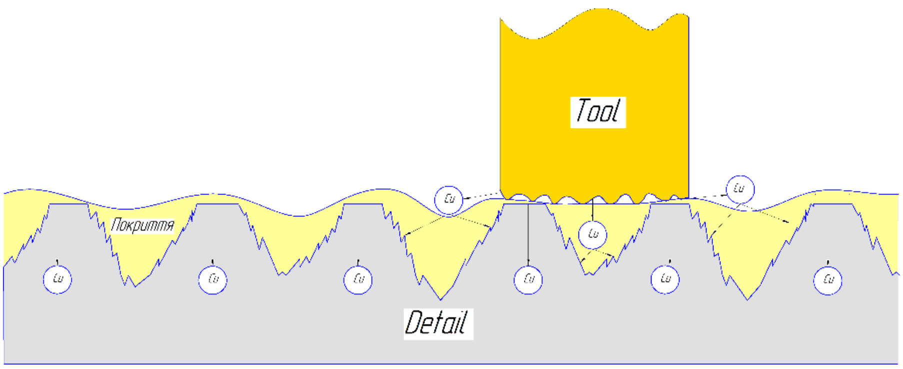

Fig. 7. Scheme of the processes involved in the formation of an anti-friction coating

The volumetric plastic flow of the tool material stops and the temperature in the friction zone decreases, which leads to inhibition of chemical reactions between the components of the process medium.

This stage is characterised by the diffusion of metal deposited on the surface deep into the surface layer of the part. Since the antifriction coatings produced by the FANT method have a certain degree of inconsistency, part of the surfactant from the process medium is adsorbed in the pores of the coating.

Conclusions

The analysis of physical and chemical processes in the contact zone ‘tool – part’ during the friction-mechanical method of applying antifriction coatings allowed to establish the following regularities:

1. For an objective assessment of the processes observed during the application of antifriction coatings, it is most appropriate to consider in detail the FANT process at the following stages: activation of the surfaces of the tool and the workpiece, deposition of antifriction components on the surface to be treated, and further formation of the antifriction coating.
2. The chemical reactions that occur during the formation of an antifriction coating allow you to track the processes of glycerol tribodestruction, copper chloride dissociation, chemical interactions of surfactants, destruction of oxide films, creation of complex compounds, etc. and identify ways to improve the quality of FANT antifriction coatings.
3. It is proved that the quality of coating formation directly depends on the material of the part and tool, temperature in the deposition zone, interaction time, material diffusion rate, and dissociation of chemical compounds.
4. The physical model of the FANT process is proposed, which illustrates chemical reactions and physical processes and allows to find out and explain the characteristic phenomena occurring at different stages of the antifriction coating creation.

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Красота А.М., Шепеленко І.В., Красота М.В. Фізичні та хімічні процеси при нанесенні антифрикційних покриттів фрикційно-механічним методом

Огляд сучасних моделей утворення антифрикційних покриттів фінішною антифрикційною безабразивною обробкою показав відсутність ґрунтовного аналізу фізичних та хімічних процесів, що відбуваються в зоні тертя. З цієї точки зору доцільним виглядає дослідження процесів утворення покриття на етапах активації поверхонь, осадження антифрикційних компонентів та формування антифрикційного покриття. Розглянуті характерні структури та хімічні реакції на різних етапах створення антифрикційного покриття дозволяють відслідкувати процеси, що відбуваються в системі, та впливати на їх. Доведено, що якість формування покриття безпосередньо залежить від матеріалу деталі та інструменту, температури в зоні осадження, швидкості дифузії матеріалу, дисоціації хімічних з'єднань. Запропонована фізична модель процесу ФАБО, яка визначає хімічні реакції та фізичні процеси, що відбуваються на різних етапах формування антифрикційного покриття. Аналіз моделі дозволяє з'ясувати та пояснити характерні явища в системі «деталь – інструмент – технологічне середовище», а, отже, впливати на якість створення антифрикційного покриття фрикційно-механічним методом.

Ключові слова: фінішна антифрикційна безабразивна обробка, фізична модель, антифрикційне покриття, технологічне середовище, активація поверхні, трибодеструкція, зносостійкість