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TOPOCHEMICAL KINETICS OF EXTERNAL FRICTION DURING MECHANICAL AND THERMAL ACTIVATION OF THE FRICTION CONTACT

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The article deals with the process of contact interaction (relative displacement) of surfaces as a chemical reaction, the regularity of which is described by the Arrhenius equation. The kinetic characteristics of Gersi-Striebeck are obtained taking into account the mechanical and temperature conditions of the frictional contact. The process of interaction of materials in friction in the form of regularities of topochemical kinetics, realized due to the processes of formation and growth of adhesion adhesion nuclei, makes it possible to present the experimental characteristics in the form of theoretical dependences. These dependences reflect the entire range of variation of the coefficient of friction from the speed of mutual movement of materials, including at ultra-low sliding speeds. In the framework of this approach, the lubricating action of the medium prevents and blocks the reactions of the transition of nuclei to actively growing nuclei.

Key words: kinetics, friction, activation, mechanical, thermal, frictional

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Introduction. The formulation of the topochemical kinetics model of adhesive grasping of two rubbing surfaces reduces to the following [3]. There are embryos and growing gripping nuclei are formed in the zone of contact spots (here the term «contact spots» refers to moving surfaces, and «gripping nuclei» refers to the topochemical adhesion reaction). The destruction of these nuclei requires the energy consumed per unit path; its dissipation is fixed as friction, which leads to the features of the realization of the process.

The formation of the set-up nuclei on the contact spots is represented as a topochemical reaction that takes place in a two-dimensional reactor. Two processes and two velocities are recorded in the model-the rate of displacement and the rate of the topochemical reaction, or two characteristic times-the running time of the two contacting surfaces relative to each other and the time of the topochemical reaction flow to a certain degree of conversion (the degree of surface coverage by the setting nuclei). The relationship between these speeds or times should determine the characteristic features of the process. Then the task of controlling the friction process is reduced to specifying the parameters of topochemical reactions – rate constants – by organizing the processes of adsorption, desorption, heat and mass transfer.

Methodology of the study. With external friction on frictional contact, formation of setting kernels occurs. At subsequent times they are destroyed as a result of the sliding of the surfaces relative to each other. This destruction creates a new surface in the energy sense – more saturated with active defects. This process can be described by the following regularity: the decrease in activation energy (nucleation of nuclei) is proportional to the speed of sliding of surfaces or some function of speed: $k_x = k_x(v)$. By analogy, for the growth rate constants of the setting nuclei, since the sites of their destruction should have an increased surface energy, which is kinetically realized at a higher rate of propagation of the reaction zone with the growth of the newly formed nucleus: $k_y = k_y(v)$.

The process of dissipation of mechanical energy must lead to the heating of the interaction zone of the surfaces due to the irreversibility of two processes: the formation and growth of clutching nuclei, on the one hand, and the destruction of nuclei, on the other. This irreversibility is reflected as a local increase in the temperature in the reaction zone $T = T(v)$.

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The rate constant of the chemical reaction is determined by the Arrhenius equation. Then the laws described above assume the form

$$k_x = k_{0,x} \exp\left\{-\frac{h^*\left[E_A^* - \delta^* g(v)\right]}{E_T^* + \rho^* g(v)}\right\}; \quad (1)$$

$$k_y = k_{0,y} \exp\left\{-\frac{h\left[E_A - \delta g(v)\right]}{E_T + \rho g(v)}\right\}, \quad (2)$$

where E_A^* – the activation energy of the transition of the embryo into an actively growing nucleus (for the initial surface); E_T^* – the thermal potential (similar to RT for the ideal gas state); g (v) is the energy conversion function; $\delta^* g(v)$ – transformation of mechanical energy into surface energy of defects; $\rho^* g(v)$ – transformation of mechanical energy into thermal energy. For this study, $\delta^* + \rho^* = 1$.

Coefficients δ^* и ρ^* reflect the conditions of the reaction zone (contact of surfaces), close to isothermal or adiabatic. Conditions close to isothermal (sufficient heat dissipation and good thermal conductivity of the material) have the meanings $\rho^* \cong 0$, and conditions close to adiabatic, $\rho^* \cong 1$ и $\delta^* \cong 0$.

For the dependence (2), analogous quantities have the same physico-chemical meaning.

Figure *1a* shows the kinetic characteristics of the process of external friction, taking into account the greater or lesser isothermicity or adiabaticity of the conditions in the zone of contact spots and the flow of topochemical reactions of formation, growth and destruction of the setting kernels (it is assumed that the relations $\delta^* + \rho^* = 1$ и $\delta + \rho = 1$ approximately fulfilled).

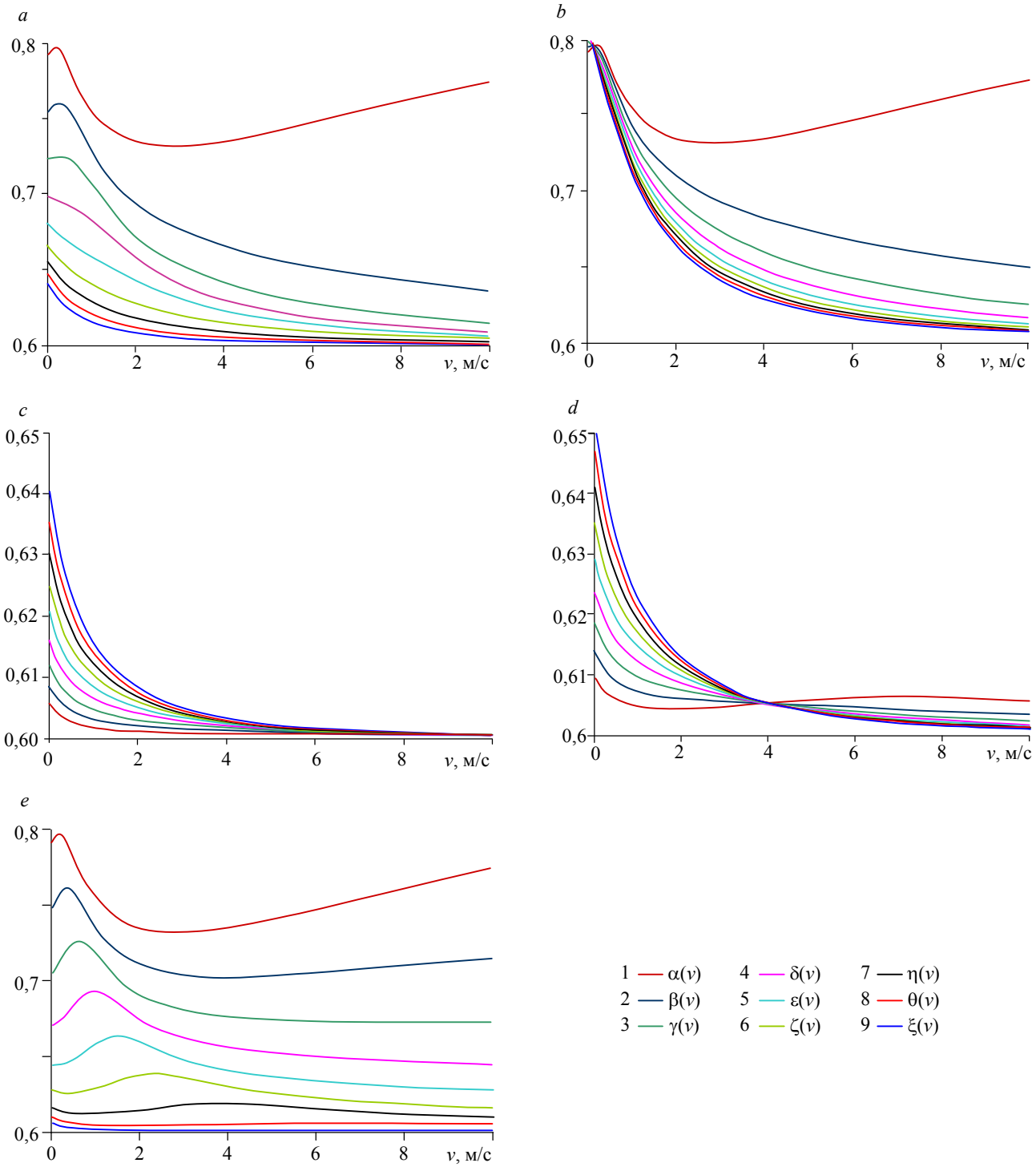
The authors [2-5] obtained, as a result of studies, transformation of equations and their integration, an analytical dependence for calculating the degree of conversion as a fraction of the surface coverage of contact spots by growing nuclei α in the following form:

$$\alpha = 1 - (1 - \alpha_0)\exp\left\{-A_0 k_y^2 t^2 \left(1 - \exp\{-k_x t\}\right)\right\}. \quad (3)$$

In this case, the following regularity is assumed: the greater the activation of the surface when the adhesion nuclei are destroyed, the less heating, and vice versa, the smaller the activation of the surfaces, the greater the proportion of external mechanical energy expended in increasing the internal energy of the system in thermal form. Thus, a large decrease in the activation energy of both processes of nucleation into nuclei and nuclear growth and a relatively small increase in temperature with increasing velocity lead to an increase in the kinetic constants and friction force or friction coefficient. These conditions, close to isothermal, give a greater value of the friction coefficient (curve 1). On the other hand, a slight decrease in the activation energy of both processes and an increase in temperature with increasing velocity (conditions close to adiabatic) give a smaller value of the frictional force or friction coefficient: curve 2 lies below curve 1, etc. The greater contribution of the dissipation of external mechanical energy to a decrease in the activation energy of the process of transition of nuclei to the nucleus reflects the parameter h^*. The value of this parameter $h^* < 1$ will reflect the inverse situation. Similar assumptions can be made within the framework of qualitative research for the parameter h.

In addition, it can be assumed that most of the mechanical energy is perceived by the contacting surfaces in the form of an increase in the specific surface energy. This leads to an increase in the concentration of embryonic nuclei (this problem has not been considered so far), as well as to a decrease in the activation energy of the transition of embryos to actively growing nuclei and the activation energy for the growth of adhesion nuclei in the contact spots (growth k_x and k_y). At the same time, it can be assumed that the thermal conductivity of the contacting materials is sufficiently high, and the temperature rise in the reaction zone is small. Here the relations $\delta^* + \rho^* = 1$ и $\delta + \rho = 1$ are not met.

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Curve	Chart				
	a	*b* ($v > 1$, $\delta^* = \delta = 0{,}9$)	*c* ($\delta^* = \delta = 0{,}1$)	*d* ($\delta^* = \delta = 0{,}2$)	*e* ($\rho^* = \rho = 0{,}1$)
1	$\delta^* = \delta = 0{,}9$, $\rho^* = \rho = 0{,}1$	$\rho^* = \rho = 0{,}1$	$\rho^* = \rho = 0{,}1$	$\rho^* = \rho = 0{,}1$	$\delta^* = \delta = 0{,}9$
2	$\delta^* = \delta = 0{,}8$, $\rho^* = \rho = 0{,}2$	$\rho^* = \rho = 0{,}2$	$\rho^* = \rho = 0{,}2$	$\rho^* = \rho = 0{,}2$	$\delta^* = \delta = 0{,}8$
3	$\delta^* = \delta = 0{,}7$, $\rho^* = \rho = 0{,}3$	$\rho^* = \rho = 0{,}3$	$\rho^* = \rho = 0{,}3$	$\rho^* = \rho = 0{,}3$	$\delta^* = \delta = 0{,}7$
4	$\delta^* = \delta = 0{,}6$, $\rho^* = \rho = 0{,}4$	$\rho^* = \rho = 0{,}4$	$\rho^* = \rho = 0{,}4$	$\rho^* = \rho = 0{,}4$	$\delta^* = \delta = 0{,}6$
5	$\delta^* = \delta = 0{,}5$, $\rho^* = \rho = 0{,}5$	$\rho^* = \rho = 0{,}5$	$\rho^* = \rho = 0{,}5$	$\rho^* = \rho = 0{,}5$	$\delta^* = \delta = 0{,}5$
6	$\delta^* = \delta = 0{,}4$, $\rho^* = \rho = 0{,}6$	$\rho^* = \rho = 0{,}6$	$\rho^* = \rho = 0{,}6$	$\rho^* = \rho = 0{,}6$	$\delta^* = \delta = 0{,}4$
7	$\delta^* = \delta = 0{,}3$, $\rho^* = \rho = 0{,}7$	$\rho^* = \rho = 0{,}7$	$\rho^* = \rho = 0{,}7$	$\rho^* = \rho = 0{,}7$	$\delta^* = \delta = 0{,}3$
8	$\delta^* = \delta = 0{,}2$, $\rho^* = \rho = 0{,}8$	$\rho^* = \rho = 0{,}8$	$\rho^* = \rho = 0{,}8$	$\rho^* = \rho = 0{,}8$	$\delta^* = \delta = 0{,}2$
9	$\delta^* = \delta = 0{,}1$, $\rho^* = \rho = 0{,}9$	$\rho^* = \rho = 0{,}9$	$\rho^* = \rho = 0{,}9$	$\rho^* = \rho = 0{,}9$	$\delta^* = \delta = 0{,}1$

Kinetic characteristics of Gersey – Striebeck; calculation by equation (3), taking into account isothermicity and adiabaticity in the zone of contact spots at $v_0 = 1$; $\alpha_0 = 0{,}6$; $A_0 k_y^2 = 1$; $k_x = 2$; $h_x = 5$; $h_y = 1$; differences are reflected in the parameters δ^*, δ, ρ^* and ρ

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In Figure *b*, the activation of rubbing surfaces is approximately equally high, and the parameters of the heat exchange of the reaction zone are different. The temperature increases slightly with increasing slip velocity, and for curves 1-9 the temperature increases with increasing speed. In this case, for increasing the kinetic frictional characteristics, the kinetic friction characteristic is fixed under conditions close to isothermal (curve 1) and falling-under conditions close to the adiabatic (curves 3-9). Similar experimental dependences are given by Akhmatov [6]. The curves in Fig. *b* illustrate the processes in which a decrease in the activation energy and an increase in temperature lead to an increase in the rate constants of the reactions.

The falling kinetic characteristic is illustrated in Fig. *c*. At the same time, as the sliding speed increases, the temperature increases and the value of the friction coefficient over the entire range of the velocity change (the position of curve 9 relative to other curves) increases. As in the previous cases, this is due to the large values of the kinetic constants and, accordingly, to the higher degree of completeness of the topochemical reaction in the region of the contact spots.

Figure *d* shows the dependencies for which, on the whole, the kinetic characteristics are incident, but an increasing kinetic characteristic (curve 1) is fixed in a certain region of slip velocities. In addition, this family of kinetic characteristics shows that at a certain fixed value of the velocity, curves inverse: the friction coefficients change the sequence of their values from one curve to the next curve. The inversion of the curves, fixed in Fig. *d*, differs from the inversion shown in Fig. *a*.

Figure *e* shows the curves for which the same contribution of external mechanical dissipation to the growth of thermal energy is characteristic and different – to an increase in surface energy in the form of a decrease in the activation energy of formation and growth of adhesion adhesion nuclei. A smaller activation energy gives a greater value of the degree of surface coverage by the setting nuclei and, correspondingly, a larger value of the frictional force over the entire range of slip velocities (curve 1 lies above curve 2, etc.).

Thus, the process of interaction of materials in friction, represented in the form of regularities in the topochemical kinetics of transformation of external mechanical energy into the internal energy of the material system and realized through the formation and growth of adhesion adhesion nuclei, makes it possible to present experimental characteristics in the form of theoretical relationships. These dependences reflect the entire range of variation in the coefficient of friction from the rate of mutual movement of materials, including the classical experimental dependence of Gersey – Striebeck, including for ultra-low slip velocities.

In the framework of this approach, the lubricating action of the medium manifests itself in the obstruction of the transition of nuclei to actively growing nuclei (a decrease in the kinetic constant k_x), as well as in blocking the growth of these nuclei (a corresponding decrease in the kinetic constant k_y). The mechanism of this action of lubricants includes the stages of sorption and mass transfer of active components (including cladding additives) that block the active center in the volume of the lubricant. Adsorption of the active components of the medium leads to a decrease in surface energy in general or to a decrease in the energy of the active centers-embryos (defects, etc.). The intensity of mass transfer also depends on the hydrodynamic component in the near-surface layer of the lubricant, the temperature, the diffusion coefficients of the active component, and other physicochemical properties of the objects participating in the friction process as a whole.

The conclusion. This approach can be developed for a theoretical representation of the growth of the frictional force of rest (the static characteristic of friction), as well as the dynamic characteristics of friction, where the frictional force depends not only on speed, but also on acceleration (positive or negative). In addition, the adopted provisions such as a linear decrease in the activation energy of the reaction of the transition of embryos to growing nuclei of adhesion setting, as well as their growth, with an increase in the slip velocity can be refined by the use of thermodynamic regularities, as well as the formulation of heat transfer problems. In its main points, this approach is consistent with the ideas [1, 9-15], which were used as the basis for constructing the static characteristic of friction, the adhesion theory of friction, and the theory of film starvation.

In the development of these theoretical representations, the authors [5, 7] carried out a more detailed qualitative analysis of this mathematical model of the topochemical adhesion adhesion kinetics.

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