Tribochemical Kinetics of External Friction

A. Yu. Albagachiev[a], *, E. A. Lukashev[b], M. I. Sidorov[c], and M. E. Stavrovskii[d]

[a]Blagonravov Institute of Mechanical Engineering, Russian Academy of Sciences,
Moscow Technological University, Moscow, Russia
[b]Soyuz Turaevo Manufacturing Design Bureau, Lytkarino, Moscow oblast, 140080 Russia
[c]Geodesic Research Institute, Krasnoarmeisk, Moscow oblast, 141292 Russia
[d]Research Center on Resource and Waste Management, Moscow, Russia
*e-mail: albagachiev@yandex.ru

Abstract—The kinetics of external friction is compared with the molecular–mechanical theory of friction. It is shown that research on the topochemical kinetics of adhesive binding is still in its early stages. Calculation methods that incorporate experimental data must be developed.

In the molecular–mechanical theory of friction, it is assumed that the lubricant films and layers absorbed on the working surfaces form a third body. As they interact with the solid bodies, these films change the properties of the surface layers, on account of the Rehbinder effect (reduction in strength by adsorption) or the Garkunov–Kragel'skii effect (selective solution of components of the solid solution). The third body is assumed to consist of several layers: (1) a boundary film varying in thickness from 2 nm (monomolecular film) to 0.1 μm (polymolecular film), which may be adsorbed or, at high temperatures, chemisorbed; (2) a film of chemical compounds (oxides, sulfides, chlorides, phosphides); (3) a thin film of crumbled particles from the base.

The ratio of the shear resistance τ of the third body to that of the base is of great importance [1]. The shear deformation will be greatest with the least resistance to the applied stress. In boundary lubrication, the shear is assumed to occur in the boundary films of lubricant; in friction without lubricant in air (in adsorbed or chemisorbed films); or in friction without lubricant in the discharged medium (in films of oxides and other compounds). The frictional contact surface is not assumed to be strictly plane. Since real surfaces are rough, with boundary lubrication, shear may also occur in boundary films of lubricant, adsorbed or chemisorbed films, and in films of oxides and other compounds. However, the shear is greatest in adhesive welds between the surfaces. All the shear processes depend considerably on the surface geometry, the load, and the physicochemical properties of the contacting materials. Together, they form a complex frictional process.

Although the formation of adhesive welds is taken into account in the molecular–mechanical theory of friction, attention focuses on the surface films, whose changes determine the frictional processes in specific tribological pairs [1].

When the lubricant contains surfactants or chemically active materials, boundary films of lubricant are formed. The viscosity of these films exceeds that of the lubricant, as a rule. This is typical of oleic and stearic acids, whose molecules are oriented perpendicular to the surface of the solid body as a result of adsorption. Materials present in the lubricant (such as diethyl sebacinate) whose molecules are parallel to the surface of the tribological components reduce the viscosity in the wall layer of lubricant.

Increase in molecular mass of the film reduces the frictional coefficient as a result of greater filling of the adsorbed layer, which is associated with the concentration of chemically active materials in the lubricant. In complex frictional conditions, the role of boundary lubricant films formed by polar organic molecules declines, while the role of oxide films increases. The influence of oxide films on the frictional coefficient is complex. In the absence of lubricant, thick oxide films increase the frictional coefficient, while thin oxide films lower the frictional coefficient.

The contacting surfaces have sections with different physical and chemical properties (adsorption enthalpy of atoms and molecules, activation energy of bond formation and rupture, etc.).

With increase in the actual contact area E_F (the sum of the contacting sections), the corresponding frictional force F increases. The size of the sections

actually in contact corresponds to a β distribution. The wear in friction (surface disintegration) largely depends on E_F, since it determines the extent of the most loaded surface layers.

The actual contact area E_F is the result of flattening of the individual surface projections on loading. Hence, greater contact deformation corresponds to greater E_F.

With actual contact of local sections of the frictional surfaces, much of the surface energy is liberated. For example, the surface energy at the metal–air boundary is about 1 kJ/m², while that in the contact zone is no more than 0.02–0.03 kJ/m². The energy liberated is an order of magnitude greater than the energy required for melting of the metal, which is 100 kJ/mol, whereas the melting enthalpy is 10 kJ/mol. Therefore, in the zones of actual contact, adhesive welds are formed.

In the analysis of friction, we need to understand the failure of the adhesive bond: failure at the bond is regarded as adhesive, and failure at greater depths as cohesive. The strength of the adhesive bond depends on the loading rate: if the loading rate changes by a factor of two, the strength of the adhesive bond changes by a factor of three [2]. Molecular bonds create normal and tangential drag. In the normal rupture of one surface from another, the molecular bonds break; by contrast, in shear, recombination occurs: that is, the failure of existing bonds is accompanied by the formation of new bonds. This results in displacement or flow.

Friction involves the deformation of thin surface layers of the contacting bodies, and is accompanied by rupture of the adhesive welds between the films or by disintegration at some greater depth if the strength of the bridge is greater than the strength of the lower layer.

The division of frictional interactions into external and internal processes reflects the classification of the rupture of frictional bonds: (1) microcutting; (2) plastic displacement of material; (3) elastic displacement of material; (4) adhesive failure of binding films; (5) cohesive failure of the basic material. Adhesive failure is regarded as external friction; the other processes correspond to internal friction.

Structural changes in the surface layer of the metal determine whether the cellular structure is disoriented or oriented. Oriented structure develops with increase in the number of deformation cycles. In monocrystalline iron, an unstable aggregation of dislocations is formed at first, constituting the cellular structure. With increase in the number of deformation cycles, this structure extends to deeper layers; larger cells appear at greater depth. The cell walls are perpendicular to the direction of friction and act as barriers to the motion of dislocations. On approaching the surface, they become stress concentrators and may lead to

microcrack initiation. In cyclic loading, they promote fatigue wear. At the surface of the frictional pair, glassy material (a metastable state) may be formed. Structural changes may lead to the formation of disperse films with no dislocations; these are characterized by a combination of developed phase boundaries, at which the crystal lattice breaks down to an amorphous state with crystalline microregions. Structure formation consists of three stages: (1) dispersion of the surface layers; (2) fine mixing of the disperse material; (3) sintering of the disperse material to form compact secondary structures at temperatures hundreds of degrees below the conventional sintering temperature outside of contact.

The change in state of the films at the surface is associated with adsorption; chemisorption; the formation of films of chemical compounds; selective transfer of frictional materials to the counterbody with friction in surfactant; and tribopolymerization. We may distinguish between external and internal adsorption effects.

(1) External effects lead to plasticization of the surface layer and adsorptive decrease in strength. They are due to the easy access of dislocations to the surface.

(2) Internal effects reduce the surface energy and induce migration of the surfactant atoms by surface diffusion at lattice defects.

The interaction of surface layers of the solid contacting bodies, lubricant, and gas in friction leads to the formation of films of secondary structure. These take two main forms (with a large number of intermediate types) [3]: (1) superplastic films that move easily over the frictional surfaces (solid solutions of the oxidants); (2) stronger, brittle, and less plastic nonstoichiometric compounds present in the contacting materials. Surfaces with films of the first type are geometrically homogeneous and are characterized by slight submicrorelief and poor wettability by the lubricant. Surfaces with films of the second type are heterogeneous at the submicro level, with smooth sections and sections of disintegrated film characterized by better wettability by the lubricant.

As a rule, films of secondary structure are in an ultradisperse state, with a large margin of free energy, in contrast to the stable state of the material. Outside the contact region, such structures are recrystallized. Their stability in friction is ensured by continually repeating loading pulses and by the diffusion of oxidants, which creates barriers for recrystallization; and also by the presence of impurity atoms, which do not form equilibrium solid solutions with the basic metal.

The surface tension at the phase boundaries in the contact zone is an important factor. As a rule, the surface tension of solids is related to the excess potential energy of the surface atoms and the kinetic energy of the electron gas in the surface layer.

In external friction, energy is dissipated in overcoming the molecular interaction (adhesion) and

deformation of the surface layer (cohesion). The frictional coefficient f includes the molecular component f_{mol} and the mechanical component f_{mech}. The molecular component is localized at a depth of $0.01\ \mu m$, while the mechanical component is observed in a surface layer of thickness $0.1\ \mu m$ or more. Therefore, the frictional process is regarded as additive: $f = f_{mol} + f_{mech}$.

The ratio of these components is $f_{mol}/f_{mech} = 1$ for rubber, 10 for polymers, and 100 for metals [1].

The molecular component of friction may be characterized by the ratio τ/σ_y, where τ is the shear resistance of the molecular bond and σ_y is the yield point of the basic material.

For the molecular component [2]

$$\tau = \tau_0 + k_{fr} p_{ac},$$

where k_{fr} is the piezocoefficient of the molecular component of friction; and p_{ac} is the actual pressure.

The third body in the frictional system has a considerable influence on τ and σ_y. Oxide films increase the yield point of crystalline bodies, for the following reasons: penetration of oxide into the microcracks; diffusion of oxygen into the crystals on deformation; obstruction of reflection and the access of dislocations; hindrance of slip at the crystal boundaries; and blocking of the Frank−Reed sources [4]. Raising the temperature has little influence on τ and σ_y up to some critical value, beyond which they decline, as a rule.

Experimental data permit the identification of the following correlation [5]

$$f_{mol} = k_1 + \frac{k_2}{h_0/h_{pr}},$$

where h_{pr} is the extent of the projections in the direction of slip; h_0 is the extent of the concavities in the same direction; k_1 and k_2 are coefficients depending on the lubricant employed.

In steady conditions, the mechanical component of friction is characterized by hysteresis losses in view of the nonequilibrium viscoelastic deformation of the material in sections of actual contact [6]. The degree of disequilibrium of this process and correspondingly the hysteresis losses depend on the ratio of the relaxation periods in the medium and in the loaded material.

The factors that basically determining f_{mech} are the coefficient k_G corresponding to the hysteresis losses; and the ratio D/r, where D is the penetration depth of a single projection (simulated by a sphere of radius r).

In the formulas proposed for f_{mech}, the mechanical component of the frictional coefficient is proportional to $(D/r)^{1/2}$ [7, 8].

As yet, there is no consensus regarding the influence of the load on the frictional coefficient [1]. The discrepancies in the results may be attributed to the different experimental conditions employed. In the case of point contact, f is approximately proportional to $N^{1/2}$ in plastic deformation, with sufficient lubricant. In elastic deformation, this relationship is weaker; with a small contact area, it is weaker still. With sufficient lubricant, f is proportional to N^j: $j = (1/5)-(1/7)$ in elastic deformation; and $j = (1/4)-(1/6)$ in plastic deformation.

With very undulatory frictional surfaces, f is practically independent of the load. In that case, the contact pressure $p_{co} = F(N^j)$, where N is the normal load; and $j < 1$. In addition, $f = F\left(p_{co}^q\right)$, $q < 1$.

The slip rate determines the form of the dependence $f = F(N)$: in the range $10^{-5}-10^{-2}$ m/s, f declines with increase in N; in the ranges below 10^{-5} and above 10^{-2} m/s, f increases with increase in N.

The two basic factors determining the external friction are the presence of direct-contact regions associated with interpenetration and mutual deformation of microprojections as the frictional pair runs in; and the formation of adhesive welds in those sections, accompanied by large local pressures at the direct-contact regions. The local pressures are large even at small loads, since the actual contact area E_{ac} is small. Since the microprojections are present at different levels, they come into contact successively as the load increases. The increase in E_{ac} is mainly due to increase in the number of actual contact regions and not in their size.

The performance of the frictional system will depend on the antifrictional number, which is the sum of the two components of the frictional coefficient

$$H_{af} = \frac{D}{r} + \frac{\tau}{\sigma_y}.$$

If H_{af} exceeds the external-friction threshold, the outcome will be the development of contact damage. If this is associated with increase in D/r, we will observe microcutting; if it is due to increase in τ/σ_y, adhesive bonding will occur. The critical value is $H_{af} \approx 2$, depending on the properties of the material and the heat treatment.

The distinguishing feature of external friction is localization of the processes associated with the shear force within a thin surface layer. Therefore, reduced shear resistance is necessary at the surface of the solid body. Formulated as a rule, this means that we need positive gradient of the mechanical properties. Accordingly, the shear strength at the surface must be lower than in the adjacent surface layer. This positive gradient may be ensured by four means: (1) the application of coatings and lubricant films; (2) the formation of protective films in the course of friction; (3) crumbling of the surface layer; (4) increase in hardness of the substrate.

As a rule, friction is regarded as a time-independent process [1]. The proposed models of frictional interaction are quasi-static. Time does not appear as a

variable in the formulas for the frictional coefficient, frictional forces, the actual contact area, the actual pressure, or the thermophysical parameters of the frictional components and the lubricant. To describe the rheological properties at contact, the time characteristics must be taken into account, as confirmed by the foregoing molecular–mechanical theory of friction, in which attention focuses on the formation and destruction of surface films, rather than on the formation and subsequent destruction of adhesive welds. However, in the theory of adhesive friction, with the formalization of topochemical kinetics, the time appears in the kinetic dependences, which reflect the influence of the slip rate on the frictional force or on the frictional coefficient at constant load and also describe the formation of adhesive welds. The destruction of the adhesive welds requires external energy. The energy consumption depends on the drag—that is, on the frictional force. However, the difference in the approaches does not rule out improvement of the mathematical models in tribochemical kinetics by means of characteristics taking account of the properties of the contacting materials.

In the general case, we use six time intervals to assess the contact rheology: four at the micro level and two at the macro level [1].

(1) The mean time for which the actual contact regions exist (or the mean duration of elementary contact): $t_{co} = h_{co}/v$, where h_{co} is the mean extent of the actual contact regions in the direction of slip. This is the time of maximum mechanical and thermal action on the material in the frictional zone, associated with wear of the third body.

(2) The mean time between actual contacts of two successive regions: $t_R = h_R/v$, where h_R is the mean distance between the actual contact regions in the direction of slip. This is the time characterized by sorptional chemical properties and cooling between the heat pulses, associated with regeneration of the third body.

(3) The mean time for wear of the film: $t_w = h/v_w$, where h is the film thickness; v_w is the mean wear rate due to desorption, mechanical abrasion, mechanochemical processes, and other processes.

(4) The mean regeneration time of the film: $t_{re} \approx h/v_{re}$, where v_{re} is the mean rate of regeneration (adsorption, flow, diffusion, etc.).

(5) The contact time of the nominal area: $t_n = h_n/v$, where h_n is the extent of the nominal contact region between two solid bodies in the direction of slip (or the nominal path length).

(6) The time between two successive nominal contact cycles: $t_D = h_D/v$, where h_D is the path to the next nominal contact.

We can only employ t_D for cyclic contacts. The parameters t_{co} and t_R are determined by the contact microgeometry and the tangential velocity, while t_w and t_{re} are determined by the microgeometry and the normal velocity

Boundary films have clearly expressed rheological properties. The wear of sorptional films is due to desorption [9]. The regeneration and wear of the films are characterized by specific adsorption kinetics [10]. In view of the nonequilibrium state of the boundary lubricant film, where the density of the adsorbed layer is significantly less than the maximum value, we must take account of the latent frictional period [4]. The latent period consists of the time for sorptional conditioning of the layer and the time for molecular reorientation. As a rule, considerable time is required for orientation of the sorbed molecular layers. The dependence of the latent period on the actual contact pressure is known. At large pressure, the latent period is considerably shortened. With increase in thickness of the thin boundary film—that is, with increase in the number of molecular layers—its lubricating properties are improved.

Dynamic equilibrium of wear and regeneration of the films defines normal friction. Friction in which wear of the lubricant, sorbed, oxide, or other films predominates over regeneration results in contact of fresh surface sections—that is, in film deficiency: $v_w t_w > v_{re} t_{re}$.

Film deficiency must be distinguished from lubricant deficiency. In both cases, however, frictional conditions become worse from first contact to final loss of contact. We observe lubricant deficiency in hydrodynamic and semiliquid lubrication with a bulk lubricant film. We observe film deficiency in boundary lubrication and in the absence of lubricant with thin films at the surface.

We assume that film deficiency is cumulative and is generally the result of repetitive damage accumulation in the third body—in other words, the result of defect accumulation in the film. There is also a possibility of film deficiency in individual contact regions, on account of a single film defect.

At high slip rates, film deficiency is due to film desorption associated with frictional heating. The duration of the temperature surge (t_{co}) is several orders of magnitude greater than the residence time of the adsorbed molecules in contact. That is sufficient for their desorption.

The adsorption–desorption equilibrium constant may be expressed in the form

$$K_E = \frac{\gamma_a \exp\left\{\dfrac{W_a}{R_\Gamma T}\right\}}{k_d \left(2\pi m_m k T\right)^{1/2}},$$

where γ_a is the adsorption probability when adsorbate particles encounter the surface; W_a is the adsorption enthalpy; k_d is the desorption rate constant; and m_m is the molecular mass.

The destruction of adhesive welds is thermodynamically irreversible, as we see in that the energy consumed to ensure the final rate of the process must be larger than the energy accumulated by the surfaces in the form of excess surface energy. Hence the endothermal process of energy accumulation is accompanied by an exothermal process of energy dissipation on account of the final tangential stress required to break the adhesive welds at a finite rate. The same considerations apply to plastic deformation of the surface layers of material (internal friction) and viscous flow of the lubricant.

Heating may facilitate desorption of the protective films, thereby permitting coverage of much of the contact spot by adhesive welds. That results in even greater heating. Further development of the process may lead to temporary dynamic equilibrium (normal frictional conditions) or to a negative trend accompanied by proliferation of adhesive welds, jamming, and scratching.

A probabilistic approach may be used to describe film deficiency, since the frictional interaction is stochastic.

The probability γ_{co} of contact through the lubricant film in contact section k at elevated slip rates depends on the ratio of the rest time t_R to the regeneration time t_{re}. At low slip rates, γ_{co} depends on the ratio of the wear time t_w to the time t_{co} for which the actual contact regions exist. If $t_R/t_{re} \gg 1$ or $t_w/t_{co} \gg 1$, then $\gamma_{co} \to 1$; if $t_R/t_{re} \ll 1$ or $t_w/t_{co} \ll 1$, then $\gamma_{co} \to 0$. In the second case, we observe cascade film deficiency if $t_R/t_{re} < 1$ and periodic film deficiency if $t_w/t_{co} < 1$. The ratio t_R/t_{re} or t_w/t_{co} determines the state of the frictional system and indicates the directionality of the process. We assume that γ_{co} may be described by formulas analogous to the Kingsbury equation for a physically absorbed film:

—at elevated slip rates

$$1 - \gamma = \exp\left\{ -\frac{t_R}{t_{re}} \right\} = \exp\left\{ -\frac{h_R}{h} \frac{v_{re}}{v} \right\};$$

—at low slip rates

$$1 - \gamma = \exp\left\{ -\frac{t_w}{t_{co}} \right\} = \exp\left\{ -\frac{h}{h_{co}} \frac{v}{v_w} \right\}.$$

As a rule, the actual contact regions are more or less elliptical, with the major axis in the direction of motion. In the calculations, it is acceptable to regard them as circular.

The parameters v_{re} and v_w depend on the properties of the films on the frictional surfaces. In boundary adhesion, they depend mainly on the properties of the lubricant layers directly at the surface (which consist of molecules oriented in the field of the solid body) and the adjacent unpolarized layers. For dry friction in air, they depend on the properties of the adsorbed and chemisorbed films (consisting of molecules of atmospheric gases, organic impurities, etc.). For friction in

a discharged medium with no lubricant, they depend on the properties of the oxide films already formed, which consist mainly of compounds formed by the metal and its impurities with oxygen.

In frictional contact, the processes in different films are interrelated. For example, in a system of two metallic bodies (Me) and also liquid hydrocarbon (RH) containing dissolved oxygen (O$_2$), oxidation is a three-stage chemical reaction:
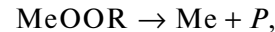
(1) radical formation by adsorption or chemisorption

$$Me + RH \Leftrightarrow MeRH;$$
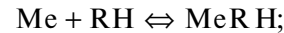
(2) the addition of oxygen to the metal–hydrocarbon-radical complex, to form a ternary complex

$$MeRH + O_2 \Leftrightarrow MeOOR;$$
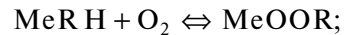
(3) breakdown of the complex to form wear particles and oxidation products of the lubricant

$$MeOOR \to Me + P,$$

where P denotes the reaction products.

In the regeneration of oxide films, v_{re} is determined by the oxidation rate v_{ox}. Oxidation is assumed to be a two-stage process:

(1) as a result of the chemisorption of oxygen by a metallic surface, oxidation proceeds in microregions and individual active centers of the surface;

(2) a crystalline oxide phase is formed.

The primary oxide film is formed practically instantaneously at the surface on the basis of crystal-chemical correspondence (epitaxy). In other words, the oxide crystals tend to reproduce the orientation and structure of the metal crystals at which they form. On account of the difference in lattice constants of the oxide and the metal, further access of free oxygen to the metal is obstructed. To ensure further growth of the oxide film, the metal ions must reach the surface, by electrical or diffusional means. In the cold oxidation of metals, films of thickness 3–5 nm are formed.

The dependence of the oxidation rate v_{ox} on the surface temperature takes the form

$$v_{ox} = k_1 \exp\left\{ -\frac{k_2}{T} \right\}.$$

Friction sharply intensifies oxidation. For carbon steel, friction increases the oxide film 200 times in comparison with a low-temperature film on an undeformed surface. The oxidation rate increases accordingly. The time for the formation of a monomolecular oxide film with friction in air is $t_{ox} \approx (1-4) \times 10^{-3}$ s.

In the regeneration of liquid lubricant layers, v_{re} is determined by the flow rate v_L. In the case of limited wetting, correspondingly, v_L is characterized by the product of the limiting angle and the time; in complete wetting, v_L is characterized by the speed of the wetting line.

In the flow of water and polar liquids, over steel, a thin primary layer outruns the bulk of the liquid flow. The thickness of the primary layer is assumed to be no more than the radius of action of the molecular attraction forces, while the thickness of the secondary layer is a few microns. Two mechanisms are proposed for the formation of the primary layer: transfer of the liquid molecules through the gas phase; and diffusion of the liquid molecules over the surface of the solid body.

We should distinguish between two types of flow: kinetic flow, in which the resistance to the flow is concentrated at the wetting line; and hydrodynamic flow, in which the resistance to the flow extends over the whole volume. As a rule, lubricant flow occurs in the first $10^{-2}-10^{-3}$ s: specifically, kinetic flow for time t_R; and then hydrodynamic flow.

The flow rate is as follows:

—with limited wetting

$$v_L = k_B P_L (\cos\theta_E - \cos\theta_D);$$

—with complete wetting

$$v_L = k_A (P_S - P_{SL} - P_L).$$

Here k_A and k_B are constants of proportionality; P_L and P_S are the surface-tension forces at the boundary with the liquid and the solid body, respectively; θ_E and θ_D are the equilibrium and dynamic limiting wetting angles; and P_{SL} is the surface tension at the solid–liquid boundary.

On the basis of the theory of absolute reaction rates, we obtain an expression for the flow rate [46]

$$v_L = J h_A \exp\left(\frac{P_L}{n_A k T}(\cos\theta_E - \cos\theta_D)\right),$$

where J is the difference between the rate J_A of direct transfer (adsorption) and the rate J_D of inverse transfer (desorption) of the liquid molecules to the solid–atmosphere interface close to the wetting line; h_A is the mean distance between the adsorption centers; n_A is the number of adsorption centers; k is the Boltzmann constant.

The intensity of the flow, determined by the number of molecules passing through unit length of the wetting line per unit time, takes the form

$$J = \frac{kT}{k_{PL}} G\left[\frac{1}{G_A}\exp\left\{-\frac{E_A}{kT}\right\} - \frac{1}{G_L}\exp\left\{-\frac{E_L}{kT}\right\}\right],$$

where k_{PL} is Planck's constant; G, G_A, and G_L are the free energies of the molecules in the active (intermediate) state, adsorbed state, and liquid state, respectively; E_A and E_L are the activation energies of the direct and inverse fluxes, respectively.

The roughness of the solid surface affects the flow. Lubricants and fatty acids form a finite limiting angle on polished steel; on a rough surface, by contrast, flow is unlimited. Flow is more rapid along channels than on a smooth solid surface [11]. The flow may be accompanied by other processes: the solution of the solid material in the liquid; diffusion of liquid components into the solid; adsorption of surfactants at phase boundaries; evaporation; chemical reactions; and crystallization.

At freshly exposed sections of the frictional surface, molecules are adsorbed from the gas or liquid phase. For example, fatty-acid molecules are bound by carboxyl groups at active centers of the solid surface and are inclined at around 90°. The next layer of molecules grows on the first so that the active ends of the molecules are in a single plane. Increase in surface concentration of the adsorbate leads to saturation of the adsorbed layer, which may be monomolecular or polymolecular. As a rule, a monolayer consists of small ordered regions with low saturation and may change its structure with increase in the saturation.

The wear and regeneration of surface films may be regarded as kinetic processes. The theory of kinetic processes is applied not only to chemical reactions but also to the fluidity, failure, fatigue, and creep of solids [12]. The rates of such processes are determined by the Arrhenius equation. The rate of formation of adhesive welds in zones of actual contact in slipping friction, with no lubricant, takes the form

$$v_F = k_Y k_F \exp\left\{-\frac{E_F}{R T_F}\right\},$$

while the corresponding rate of destruction of adhesive welds is

$$v_U = k_U \exp\left\{-\frac{E_U}{R T_U}\right\}.$$

Here k_Y, k_F, and k_U are empirical coefficients; E_F and E_U are the activation energies of regeneration and wear, respectively; T_F and T_U are the temperatures of regeneration (the surface temperature in the frictional zone) and wear (the sum of the surface temperature and the temperature surge in zones of actual contact), respectively.

The coefficient taking account of the film's loss of performance in the course of friction takes the form

$$k_Y = k_{Y0} \exp\{-k_{Y1} C_{am}\},$$

where k_{Y0} and k_{Y1} are constants; C_{am} is the concentration of active material in the film.

The activation energy of film deficiency is calculated as the difference

$$E_{fd} = E_U - E_F.$$

We may determine E_{fd} from the slope of the dependence of $\ln L_0/L_k$ on $1/T$. The proposed method may be used in situations where the temperature in the frictional zone is not measured but only the ratio L_0/L_k. (The method of temperature calculation was outlined in [13].)

In investigating the lubricants in boundary lubrication, the primary task is to determine the rate constants of film destruction and regeneration. The formal apparatus of chemical kinetics is used to determine those rate constants. We assume that, in the given model of friction in hydrocarbon lubricants, the main chemical reaction is oxidation with the participation of molecular oxygen, while the reaction of the metal with additives is a competing reaction. The wear products are inorganic metal compounds. Therefore, the model assumes that wear is due to the destruction of secondary structures. However, wear of the metal in the subsurface layers is assumed to be possible in certain frictional conditions; the resulting metal particles form inorganic compounds practically instantaneously in the frictional zone [1].

The relative wear rate v_{UF} of the third body (the ratio of the wear rates in the additive solution and in the basic lubricant), which is regarded as the resultant of the wear rate v_U and the regeneration rate v_F, may be calculated from the formula

$$v_{UF} = 1 + \frac{k_F C_{am}^v (k_U - 1)}{k_F C_{am}^v + k_U}$$
$$\times \left[1 - \exp\left\{ -k_U \frac{k_F C_{am}^v + k_U}{k_U C_{am}^v + 1} t \right\} \right].$$

With a long frictional process ($t \to \infty$), we may write

$$v_{UF} = 1 + \frac{k_F C_{am}^v (k_U - 1)}{k_F C_{am}^v + k_U}.$$

With a high concentration of active materials in the film, we note an extremum of v_{UF}

$$v_{UF} = \frac{1}{k_F C_{am}^v} + k_U - 1.$$

Today, tribological theory is based on mathematical models and precision experiments that allow frictional effects and wear to be distinguished. Many manufacturing breakthroughs have become possible with the discovery of hydrogen wear, wear-free friction, and selective transfer. In view of the complexity of frictional processes, specialists in the design, operation, and servicing of manufacturing equipment must face challenging problems. For example, the lack of a general approach prevents the development of selection principles for the materials used in frictional pairs and the composition of lubricants on the basis of their primary physicochemical characteristics [14–16]. A complicating factor is that materials science is a rapidly developing science, and new alloys and materials are constantly being developed, although their industrial adoption is delayed by prolonged frictional and wear tests. The current theories of friction and wear are based on empirical and semiempirical formulas, which are of limited practical applicability since their

coefficients must be empirically determined in each specific case. Therefore, bench tests are required at the design and development stages before industrial introduction is possible.

Research shows that physicochemical analysis of frictional pairs and lubricants cannot unambiguously determine their frictional and wear properties. The division of friction into dry, boundary, mixed, and hydrodynamic processes is somewhat arbitrary and not entirely justifiable. Tribological theory is based largely on mechanical parameters and empirical formulas. In the adhesive and molecular–mechanical theories of friction, means of distinguishing between external and internal friction have been developed. The physicochemical analysis of the action of metal-coating additives, for example, is fundamentally qualitative and is of assistance in attempts to reduce the volume of tribological experiments required. Mathematical models of friction—in particular, the topochemical kinetics of adhesive binding—are still at the design stage and requires the development of calculation methods that incorporate experimental data.

To a large degree, practical research still underlies the analysis of chemical reactions in friction and wear. The lack of sound theoretical principles slows scientific progress in the field and its practical application. Theoretical tribology must rely on precise and reliable experimental data. Processes that occur with variation in the relevant external and internal factors may be described by determinist formulas or statistical correlations. However, the diversity of phenomena responsible for wear complicates the construction of mathematical models for the prediction of such processes.

REFERENCES

1. Kragel'skii, I.V. and Gittis, N.V., *Friktsionnye avtokolebaniya* (Friction Auto-Oscillations), Moscow: Mashinostroenie, 1987.

2. Deryagin, B.V., Krotova, N.A., and Smilga, V.P., *Adgeziya tverdykh tel* (Adhesion of Solids), Moscow: Nauka, 1973.

3. *Poverkhnostnaya prochnost' materialov pri trenii* (Surface Strength of Materials in Friction) Kostetskii, B.I., Ed., Kiev: Tekhnika, 1976.

4. Akhmatov, A.S., *Molekulyarnaya fizika granichnogo treniya* (Molecular Physics of Boundary Friction), Moscow: Fizmatlit, 1963.

5. Kragel'skii, I.V. and Gittis, N.V., Evaluation of frictional properties of thin films of lubricants, *Dokl. Akad. Nauk SSSR*, 1982, vol. 265, no. 5, pp. 1125–1127.

6. Teodorovich, E.V. and Dobychin, M.N., Hysteresis losses due to friction, *Trenie Iznos*, 1980, vol. 1, no. 5, pp. 824–830.

7. Mikhin, N.M., *Vneshnee trenie tverdykh tel* (External Friction of Solids), Moscow: Nauka, 1977.

8. Kragel'skii, I.V., Dobychin, M.N., and Kombalov, V.S., *Osnovy raschetov na trenie i iznos* (Calculations for Friction and Wear), Moscow: Mashinostroenie, 1977.

9. Bowden, F.P. and Tabor, D., *The Friction and Lubrication of Solids*, New York: Oxford Univ. Press, 1950.

10. Holm, R., *Electric Contacts Handbook*, Berlin: Springer-Verlag, 1958.

11. Lozovskii, V.N., *Nadezhnost' gidravlicheskikh agregatov* (Reliability of Hydraulic Aggregates), Moscow: Mashinostroenie, 1974.

12. Yokobori, T., *The Strength, Fracture and Fatigue of Materials*, Groningen: P. Noordhoff, 1965.

13. Chichinadze, A.V., *Raschet i issledovanie vneshnego treniya pri tormozhenii* (Calculation and Analysis of External Friction during Braking), Moscow: Nauka, 1967.

14. Lukashev, E.A., Stavrovskii, M.E., Oleinik, A.V., et al., *Tribokhimiya vodorodnogo iznosa: monografiya* (Tribochemistry of Hydrogen Wear: Monograph), *Kursk*: Kursk. Gos. Tekh. Univ., 2007.

15. Lukashev, E.A. and Stavrovskii, M.E., Construction of mathematical models for technical diagnostics of friction units, *Teor. Prikl. Probl. Servisa*, 2004, no. 1 (10), pp. 10−19.

16. Albagachiev, A.Yu. and Zuev, V.V., *Effektivnye tekhnologicheskie metody obespecheniya kachestva detalei mashin* (Efficient Technological Support of Machine Parts Quality), Moscow: Mosk. Gos. Univ. Priborostr. Inf., 2013.

Translated by Bernard Gilbert