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O.I. Bohdanovych, PhD (National Aviation University, Ukraine)

Tribokinetic test algorithm

An algorithm of tribokinetic tests for determination of kinetic characteristics (order and rate constants) and activation energies of three stages of the three-stage reaction has been developed, which makes it possible to propose an energetic activation matrix as a complex criterion for assessing the wear resistance and compatibility of triboconjugtions.

In the case of boundary lubrication, the metal contact of the friction bodies can be limited by formation of lubricating boundary layers of different origin on the friction surfaces. They are formed as a result of interaction of the working surfaces activated by friction process with the active lubricant components [1]. The ability of lubricant to form strong boundary layers of sufficient thickness in short periods of time largely determines the durability of heavy-loaded triboconjuctions that operate continuously or periodically in a boundary lubrication mode [2]. Among the known models of formation and destruction of boundary layers, kinetic models occupy an important place as they allow description of the relationship of thermodynamic and kinetic parameters for processes of formation and destruction of boundary layers in terms of the load parameters.

Kinetic models of boundary lubrication can be divided into four groups:

- models of destruction of boundary layers due to loss of active components by lubricating medium;

- models of formation of boundary layers during the tribological process;

- models of transition to seizing due to excess of the rate of boundary layer destruction over the rate of its formation;

- models of wear under boundary lubrication [1].

I. Langmiur, W. Biukhe and B.V. Deryagin [2] have found that the lubricant involved in tribological process is gradually worn out and can no longer perform its functions, because its active components are adsorbed on the wear products and carried away with them from the contact or interact with the metal surface due to tribological transformations under the action of thermal energy generated by friction and the catalytic effect of new exposed metal surface (Group 1). In such cases, the antiseizing properties of lubricant do not play a decisive role in providing a friction unit with high efficiency. In [3], a method has been developed to assess the kinetic characteristics of this process taking into account that seizing occurs when the rate of conversion of lubricant to non-lubricating products, V_{np} , exceeds the rate of lubricant entering the friction zone, V_n . The rate of lubricant decomposition is estimated by the Arrennius law:

$$gV_{np} = A - (E/2,3RT),$$
 (1)

where A is a constant; T is the absolute temperature in the tribological contact; E is the activation energy of the tribological test process; R is the gas constant.

The relationship between V_{np} and the velocity of relative displacement of friction bodies, V_n , can be expressed by the equation:

$$V_{\rm np} = V/L, \tag{2}$$

where L is the length of the Hertz contact estimated graphically by the parameter of approximation of the linear dependence $\ln(V/L) - 1/T$.

Thus, it is possible to determine the activation energy E of the lubricant degradation process as a product of the gas constant R by the tangent of angle of line slope to the abscissa axis.

Models of formation of boundary layers during the tribological process (Group 2) are rather simplified and designed not to describe the tribological process but rather to assess its kinetic characteristics in order to optimize either the lubricant composition, or the tribological contact microgeometry.

In [3], a kinetic equation for calculating the activation energy of the modified layer formation has been derived on the basis of comparison of the time required for the modified layer in the contact to achieve a thickness sufficient for marked decrease in the friction coefficient and replacement of intense adhesive wear with milder corrosion-mechanical wear with the time between successive contacts of micro-inequalities, during which the growth of this layer is possible. The model makes it possible to assess the temperature of the beginning of effective action of chemically active additives and the maximum temperature at which boundary lubrication completely loses efficiency. In this regard, it should be noted that testing lubricants at low temperatures can distort their true antiwear properties in the conditions of boundary lubrication.

Models of transition to seizing (Group 3) when the rate of destruction of boundary layers exceeds the rate of their formation can be divided into two groups. The first includes models based on the idea that the destruction of the boundary layer is sufficient for seizing the friction unit. Models of the either group assume that for seizing it is necessary to achieve a critical cycle of adhesive bonds between the contact surfaces in the areas of metal contact formed due to the boundary layer destruction; herein an increase in the number of these bonds is considered as a kinetic process.

These models can be classified by the origin of the boundary layer, the destruction of which is one of the necessary steps for the appearance of seizing. The boundary layer destruction occurs due to the competition of adsorption and desorption of surfactant molecules. The destruction of a modified layer is considered to be kinetic, and its rate is controlled by chemical kinetics. Seizing of triboconjugations occurs at a temperature when the rate of destruction of the modified layers exceeds the rate of their formation. Heating causes thermal decomposition of the modified layers with the rate described by the Arrhenius equation.

Kinetic models of wear with boundary lubrication (Group 4) have been studied well enough. Since the primary step in the formation of boundary layers is adsorption of active components of the lubricant on the friction surfaces, it can be expected that in the case of low loads and low contact temperatures, adsorptionbased wear models may be effective. The Kostetsky kinetic model [4] includes three stages: (1) adsorption of reagent molecules on friction surfaces; (2) interaction of these molecules with the metal surface layer resulting in formation of a modified layer; (3) destruction of the layer with the exposure of the activated metal surface ready for further interaction with the environment. Based on this, the following equation was proposed to estimate the intensity of mechanochemical wear under boundary lubrication:

$$I = 2h_{\rm M}\gamma k^{\rm p} \sqrt{\frac{(Sh_{\rm M}/Gh_{ad})k_1^{A}}{k_2^{D} + k^{\rm M}}},$$
(3)

where $h_{\rm M}$ is the thickness of the modified layer; γ is the specific mass of secondary structures; $k^{\rm p}$, k_1^A , k_2^D , $k^{\rm m}$ are rate constants for destruction, adsorption, desorption and modification, respectively; *S* is the contact spot area; G stands for adsorption; $h_{\rm ad}$ is the adsorption layer thickness.

The longevility of friction units is significantly affected by organic deposits. It is known that during friction in the mode of boundary lubrication, such kinds of layers are formed on the surfaces: a layer of physically adsorbed lubricant molecules bound to the surface relatively weakly (*A*-layer); chemisorption layer, strongly bound to the surface of organic deposits formed mainly by oxidation and destruction of lubricant (*D*-layer) as well as a chemically modified layer on the base metal formed through direct chemical reactions of the metal with additive molecules (*M*-layer) [5,6].

The formation of protective layers and secondary structures as well as the emergence of dislocations to the surface are elements of self-organization of the tribosystem in which a friction pair and a lubricant are involved. Therefore, friction is a classic example of an unbalanced process, which can be considered in terms of the theory of self-organization of irreversible processes [7]. Of the seeming chaos of processes that occur during friction, those of them attract attention first of all that take place in any case, namely the phenomena of wear and formation of secondary structures (or phenomenon of structural adaptation to friction).

Stabilization of friction parameters and reduction of wear are accompanied by formation and stabilization of the composition of secondary structures that perform protective functions, limiting the spread of interaction inside solids and preventing their direct interaction. The tribosystem seeks to concentrate all types of interaction in thin surface layers. According to Kostetsky [8], from 90 to 98% of friction energy is accumulated in secondary structures, so they are a zone of predominant energy dissipation.

In the process of friction, the body can be supplied with such an amount of energy that does not have enough time to dissipate throughout the body of friction via thermal and electrical conductivity, diffusion, etc. This can lead either to catastrophic wear due to seizing, or to the appearance and development of secondary structures near the friction surface, formation of which leads to redistribution of energy in the friction body. There are three states of the friction body absorbed the same amount of energy:

1. Equilibrium state: energy is uniformly distributed; the body entropy is maximum.

2. Stationary state with no secondary structures: there is redistribution of energy, which varies according to a monotonically decreasing function depending on

the distance to the friction zone. The entropy is reduced in comparison with the equilibrium state due to the non-uniform distribution of energy.

3. Stationary state with secondary structures: there is redistribution of energy in the direction of greater non-uniformity in such a way that most of the energy is concentrated in a narrow zone of secondary structures up to several tens of microns; the rest of the energy is distributed throughout the body according to a monotonically decreasing function. Entropy at the same energy level decreases to a greater extent than in the absence of secondary structures. Therefore, the process of formation of secondary structures, which usually leads to a decrease in the coefficient of friction and, consequently, in the intensity of wear, corresponds to self-organization processes and formation of dissipative structures. Secondary structures are stable protective formations on the friction surfaces. Their composition is determined by the composition of the friction pair materials.

Thus, the protective functions of tribosystem determine its ability to adapt to external effects. The essence of the phenomon of structural adaptability is that in its implementation, all interactions of friction bodies with the environment are localized in thin layers of secondary friction structures formed on the initial materials due to their structural rearrangement and interaction with the environment [7].

As another phenomenon that is characteristic for any friction process, the destruction of surface may be considered. Under friction, material is not destroyed, but transformed into some structures that perform protective functions. Bershadsky [9] has shown that the minimum wear intensity corresponds to the region of minimum production of the tribosystem entropy.

Subsequently, the author developed a kinetic model of normal mechanochemical wear under a boundary friction, which is presented in Fig. 1 as a three-stage tribokinetic autocatalytic reaction [10].

$$Me^{0} \longrightarrow RB \stackrel{A}{\longleftrightarrow} Me_{x_{1}}(RB)^{*}_{y_{1}} \xrightarrow{M} Me_{x_{2}}B^{*}_{y_{2}} \xrightarrow{P} Me_{x_{3}}B_{y_{3}} \longrightarrow Me^{0}$$

Fig. 1. Scheme of three-stage tribokinetic autocatalytic reaction: Me^{θ} are juvenile areas of the metal surface; RB is the lubricant (R is the hydrocarbon radical; B is the active component of the lubricant); A stands for the adsorption stage; M – for the modification stage; Me are juvenile areas of surfaces of contacting structural materials of triboconjuction; $Me_{x_1}(RB)_{y_1}^*$ denotes the adsorption complex; $Me_{x_2}B_{y_2}^*$ – the complex of modified secondary structures active against the stage of destruction (P); $Me_{x_3}B_{y_3}^*$ are wear products of surface destruction, that is, triboreaction products. The indices $x_{i_0} y_i$ denote the partial coefficients of the components.

From the triboreaction in Fig. 1 it follows that only the first stage, i.e. adsorption A, is reversible (bilateral). The other stages are considered to be irreversible (unilateral). Juvenile areas of contacting structural materials act as an initial reacting component and a catalyst of triboreaction, which accelerates the first stage A. The total juvenile area (concentration Me) with normal (stationary) wear remains constant, while the amount of initial materials gradually decreases because of wear. The amount of lubricants and structural materials is considered to be large

enough, and their concentration does not depend on the triboreaction duration. Otherwise, their absolute amount rather than concentration should be used [10].

Conclusion

The three-stage tribokinetic autocatalytic reaction proposed by the author allowed him to develop a computational-experimental method for assessment of kinetic and energy-activation characteristics of wear resistance of triboconjuction materials, which makes it possible to experimentally study the regularities of change in the activation energy of three stages of surface destruction under normal wear and thus to deepen the idea of the energetic nature of structural compatability of materials during friction.

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