Tribology in Industry

Algorithm for Tribokinetic Modeling Tests of Triboconjuction Materials for Industrial Products

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A B S T R A C T

An experimental-calculation procedure for determining the kinetic and energy activation criteria for assessing the wear resistance and compatibility of triboconjunction materials using the kinetic three-stage triboreaction is presented. The developed method for tribo-kinetic tests to determine the kinetic characteristics (order and rate constants) and activation energies for all three stages of the triboreaction was tried experimentally for steels ShKh-15 and 45, aviation fuel RT, aviation hydraulic oil AOH-10 and aviation oil MK-8 added with oleic acid. The conducted tribo-kinetic tests established kinetic and activation energy criteria for assessing the wear resistance of ShKh-15 steel and antiwear properties of RT and AOH-10 lubricants, as well as kinetic criteria for assessing the wear resistance of steel 45 and antiwear properties of MK-8 with oleic acid. Also, using the developed method for tribokinetic tests, the kinetic and activation energies of ShKh-15 in long-term storage aviation fuels "TS-1" and "TS-1*", kinetic criteria and activation energy for the second stage of the triboreaction, chemical modification ShKh-15 in the medium of "TS-1", as well as the established kinetic and activation energy of the triboreaction, that is, surface destruction, in fact, wear of steel 45 during reciprocating motion.

1. INTRODUCTION

Acceleration of scientific and technological progress, as applied to industry, provides an increase in the quality, reliability, efficiency and productivity of machines, mechanisms, equipment and other industrial products. The solution of this problem relative to friction units of machines and mechanisms is impossible without unified modeling tests and the accumulation of the data bank of their results. At the same time, the criteria for assessment of the processes under study are of particular importance, since the effectiveness of the use of any algorithm for tribological modeling tests fundamentally depends on the invariance and constructiveness of the selected criteria for estimation of the studied processes. In this

regard, the development of fundamental invariant energy criteria for assessing the wear resistance and compatibility of structural and lubricating materials and the corresponding methods for obtaining unified data has become extremely important in tribological engineering.

As such criteria, such kinetic characteristics have been studied as constants of the rate and activation energy for the determining processes in tribo-systems.

The basic requirements for these criteria are their invariance (independence of the loading conditions) and commonality for structural and lubricating materials, which makes it possible to select their compatibility (optimal combinations) [1].

The aim of the work is to develop an algorithm (methodology) for tribological modeling tests of structural and lubricating materials of tribo-conjunctions using such kinetic characteristics as constants of the rate and activation energy of the determining processes (significantly slow) in tribo-systems.

2. PROBLEM STATEMENT

Today most physical processes are known to mankind in the process of friction, such characteristics should be integral, energy material scientific for triboconjunction materials. For example, in the structural-energy theory of friction and wear and the theory of structural adaptability of triboconjunction materials, the following characteristics are used: the specific work of destruction – A_p [2], energy consumption of the friction system on the thermal index – « EFSq » [2], critical friction value – A_{cr} [2], critical (boundary) density of internal energy – U^*, (for abrasive wear) [3], surface energy or surface tension - γ [4], work of the electron output WEO [4], exoelectronic emission – EEE [4], contact potential difference – U_{CPD} [4]. At the meantime, the energy characteristics of wear resistance characterize the processes of surface destruction, substantiate the evaluation of friction conditions, the choice of materials for triboconjunctions, their combination within normal wear (without damage) determine the limits of transition to damage.

The indicated criteria are not direct characteristics of the wear resistance of the triboconjunction materials. Thus, the most commonly used, best-studied and experimentally tested criterion - the specific work of surface fracture (the ratio of frictional force to wear) which is the imaginary characteristic of wear resistance and depends not only on the surface strength of the material, but also on the ability of the tribo-system to dissipate energy. Usage of surface energy γ is too complicated due to the lack of reliable data on the magnitude γ for pure metals, and moreover for alloys in real conditions [4].

Energy compatibility assessment criterion which is either surface energy or surface tension γ, or work of the output of the electron etc., as well as the criteria for wear resistance, are not direct compatibility characteristics. In addition, there is no reliable data γ even for pure metals, γ and different values of electron output work for different faces of the crystal [4].

The most direct, quantitative, structural-energy (material-science), kinetic (physical-chemical) characteristic that is useful for assessing wear resistance of triboconjunction materials is the activation energy of surface deterioration (wear) E_p, which characterizes the potential barrier to the implementation of elementary acts of destruction [5]. At the same time, in the range of structural adaptability of triboconjunction materials E_p must be invariant [5, 6], which can be used as a criterion for assessment the anti wear properties of the lubricants [7]. This, in contrast to the existing variety of criteria for assessing wear resistance, is regulated by *GOST* 9490-75 and *GOST* 23.002-78, allows usage of the E_p as a single universal criterion for evaluation of tribological properties of triboconjunction materials.

Versatility E_p is confirmed by its application as a criterion for evaluating various physical processes. An example is the application of activation energy U as functions of resistance to deformation of a plastic deformable metal sample. In the meantime U which describes the processes of rearrangement of atoms in a crystal lattice, determines the degree of violation of the order that causes deformation [8]. Despite the coincidence of values of activation energy U of diffusion and self-diffusion [9], as well as confirmation of equality $U \cong 20RT_{Mp}$, where T_{Mp} is Melting point [10], and this conclusion does not provide confident results due to the low accuracy of the degree of violation of the order of the crystal lattice.

However, even the correct choice of criteria for assessing the wear resistance and compatibility of triboconjunction materials does not guarantee the correct determination of wear resistance and compatibility of these materials.

The correct choice of the criteria for assessing wear and compatibility is a necessary condition, but not a single one. An adequate condition for the correct assessment of wear resistance and compatibility of triboconjunction materials is the correct method for assessment of wear resistance and compatibility of these materials.

3. RESEARCH'S CONSIDERATION

Nowadays three methods for evaluating the activation energy are known: 1) Graphic [9,10,11, 12,15]; 2) Extrapolation [16]; 3) Kinetic [7,13, 14,17,18]. In the first method the value of E^d depends on the scale of the coordinate system. Therefore E^d can only be used in comparative trials [18]. In the second method of meaning E^d depends on the subjective qualities of the researcher since extrapolation is an approximation of the values $f_{(x)}$ in points x lying outside the segment (x_o, x_n) by their values at points $x_o < x < ... < x_n$. However, the best and the most precise technique is the third one -kinetic, where the value E^d is determined by the laws and the equation of chemical kinetics, when first the order of the chemical reaction determined, then the constant of the rate of this reaction at least at two temperatures reaction are either determined and finally E^d is calculated using the Arrhenius equation [7]. This allows to calculate the accuracy of the determination of kinetic parameters (order and rate of reaction) and E_p according to statistical laws and equations, which considerably increases the constructivity of these criteria and confirms the possibility of their use as criteria for the assessment of wear resistance and compatibility of triboconjunction materials. However, the kinetic technique was developed on the basis of a kinetic, three-stage model of normal mechanical and chemical wear, for the description of which the following scheme of the tribological reaction (tribo-reaction) is used:

$$RB \xleftrightarrow{A} Me_{x1}(RB)^*_{y1} \xrightarrow{M} Me_{x2}B^*_{y2} \xrightarrow{D} Me_{x3}B^*_{y3} \xrightarrow{D} Me^o \quad (1)$$
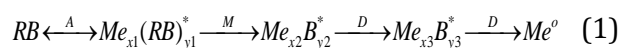
Where RB – lubricant that takes part in a three-way reaction: in the simplest case only the effect of the active component of the lubricant-additive can be considered, therefore RB is an active component of the lubricant (additive), R – hydrocarbon radical additive, B - active component of the additive, Me^o – juvenile surfaces of contact surfaces of triboconjunction materials; X_i, Y_i – partial coefficient of components, which are analogs of stoichiometric coefficients in true chemical reaction.

The following active complexes of a tribo-reaction are marked by the asterisk:

$Me_{x1}(RB)^*_{y1}$ - Adsorption complex formed as a result of the adsorption of the lubricant RB on the juvenile sections of the surfaces of structural triboconjunction materials Me^o. This complex is active in relation to the next stage - chemical modification;

$Me_{x2}B^*_{y2}$ - modified (dissipative secondary) structures, active in relation to the stage of surface destruction P;

$Me_{x3}B^*_{y3}$ - A complex of surface destruction (products of wear), in essence - a product of a tribo-reaction.

As it can be seen from tribo-reaction (1), only the first stage adsorption A is considered as a reverse, i.e. two-way one. Other stages are considered to be substantially reversible, i.e. one-way ones. The juvenile areas of contacting structural materials are both an initial reactive component and a catalytic tribo-reaction, which accelerates the course of the first stage A. In this case, the total area of juvenile sections, which is the concentration Me^o in normal (stationary) wear it remains constant [19], while the amount of output materials is constantly decreasing as a result of wear. The amount of lubricating and construction materials is assumed to be sufficiently large and their concentration does not depend on the duration of the triboreaction. Otherwise, it is necessary to use absolute values rather than concentrations.

According to the above-described kinetic three-stage model of normal mechanical and chemical deterioration, it is necessary to develop an experimental calculation method for evaluating the kinetic characteristics and activation energies of all three stages of a three-way reaction.

Paradoxically it is necessary to determine firstly the kinetic characteristics and the activation energy of E_d – a third, the last stage of the three-action that is, actually a wear itself as the result of conducting tribo-kinetic trials of materials tribo-conjunctions.

The ball segments V_w are chosen by means of measuring the diameter of the spots of wear of three balls and the amount of wear is calculated. After conducting similar tribo-kinetic tests at 4-5 values of the duration of such tests t, we construct the dependency schedules lgV_w from the duration of the test t. The straight lines of such graphs indicate the first order of the investigated stage (in this case, the third stage of the tribo reaction), i.e. $N_d \cong 1$ while a tangent of an angle of inclination to the abscissa axis of a graph determines the speed constants of the investigated stage, in this case K_p. However, the graphical evaluation and the values of the order and the rate constants of the studied tribo-reaction steps gives approximate results only. Therefore, more accurate values of these kinetic characteristics should be determined analytically, i.e. determine using the required formulas. For example, the order of the study stage, that is the third one is calculated by the following formula (2):

$$N^d = \frac{\lg \dfrac{W_2}{W_1}}{\lg \dfrac{V_{wt_{i+1}}}{V_{wt_i}}} \qquad (2)$$

Where W_1 and W_2 are the speeds of stage III i.e. the wear determined for the intervals of tribo-kinetic tests calculated via formulas (3) and (4):

$$\Delta t = t_{i+1} - t_i \qquad (3)$$

Where

$$W_1 = \frac{V_{wt_{i+1}} - V_{wt_i}}{\Delta t} \qquad (4)$$

Where $V_{wt_{i+1}}$ and V_{wt_i} are the wear volumes of three balls during tribo-kinetic tests at the duration of t_{i+1} and t_i respectively.

The order of stage III can be calculated by two ways for each:
1) Calculation for each interval Δt and then calculate the arithmetic mean N_i.

2) Calculation of Δt start and end intervals while, N_d is calculated during the entire duration of tribo-kinetic tests.

The rate constant of stage III, wear was calculated using the difference V_w in the interval Δt by the formula (5):

$$K^d = \frac{\Delta V_w}{\Delta t V_{w.m}} = \frac{W}{V_{w.m}} \qquad (5)$$

Where $V_{w.m.}$ is the average value of V at the beginning and end of the interval Δt.

By setting a minimum 4 value of K_d, it is possible to perform statistical processing of the obtained results, i.e. to calculate the average values of K_d, the confidence interval of the estimation K_d-ΔK_d, and Z_c - the coefficient of variation of that estimation.

Repeating tribo-kinetic tests according to the above procedure at another value of temperature different from T_1, according to the Arrhenius equation we calculate the activation energy of the third stage of the *TR* - the actual wear of the tribo- materials.

In addition, a following formula (6) is proposed by an author for calculating the area of secondary structures participating in the *TR* (S_{ss}) [20] and as a consequence, the calculation of the relative area of the secondary layers,

$$\delta = \frac{S_{ss}}{S_f} \qquad (6)$$

Where S_f the area of contact, i.e., the contact area of the three spots of allowed to calculate the kinetic characteristics (N_M, K_M) and activation energy of the second stage of *TR*-chemical modification (E_M) using the formula (7):

$$S_{ss} = S_f - \frac{\Delta V_{w.m}}{\Delta t h_{ss} K^d} \qquad (7)$$

Where $\Delta V_{w.m} = V_{wt_{i+1}} - V_{wt_i}$ is the wear volume of three balls in the interval $\Delta t = t_{i+1} - t_i$ in respectively; $h_{вc}$ is the thickness of the secondary structures or the thickness of the chemical modification. This value is variable: with the increment of the duration of tribo-kinetic tests $h_{вc}$ decreases.

Kinetic characteristics of the first stage of $TR(Na, Ka)$ and the activation energy can be determined by performing tribo-kinetic tests using the specified algorithm with a chemical-active substance, i.e. an additive, such as oleic acid [21], which allows to determine the kinetic parameters and the activation energy of tribo-sorption on the activation of a chemical substance.

These tribo-kinetic tests were performed at a single fixed temperature T_1. If similar tribo-kinetic tests are performed under a different temperature T_2 different from T_1, then the values of similar kinetic criteria N and K of the three stages of TR are obtained. Knowing the value of K at two temperatures T_1 and T_2, the activation energies of these stages are calculated according to the Arrhenius formula (8):

$$E = \frac{RT_1T_2}{T_1 - T_2} \ln \frac{K_2}{K_1} = \frac{1{,}9144T_1T_2}{T_2 - T_1} \lg \frac{K_2}{K_1} \times 10^{-2} \quad (8)$$

Where K_1 and K_2 are the rate constants at temperatures T_1 and T_2 respectively, 1.9144 is the product of the gas constant R = (8.3143 ± 0.0012) x10^3 $j/K \cdot mol$ by the module of conversion of natural logarithms to decimals, which is equal to 2.3056.

In addition, in case there is a possibility to calculate the wear amount of the moving element of the triboconjunction, then the fourth value of activation energy of the value E_{d_d} (E^a, $E^м$, $E_{d_{nd}}$ and E_{d_d}) is obtained. Therefore, the four values of E constitute the matrix criterion for evaluating the durability and compatibility of tribomaterials

$$\begin{vmatrix} E^a & E^м & E_{nd}^d & E_d^d \\ E_1^a & E_1^м & E_{nd1}^d & E_{d1}^d \\ E_2^a & E_2^м & E_{nd2}^d & E_{d2}^d \\ E_3^a & E_3^м & E_{nd3}^d & E_{d3}^d \\ E_n^a & E_n^м & E_{ndn}^d & E_{ndn}^d \end{vmatrix} \qquad (9)$$

where $E_{d_{nd}}$ and E_{d_d} are the activation energies values of the materials surface fracture for the both fixed and movable tribocoupling elements, respectively; "A", "m" and "d" are the activation energies of tribo adsorption, chemical

modification, and surface destruction respectively, i.e. the actual wear of the tribo coupling elements of both mobile and stationary ones.

The investigation of tribo-kinetic study of the tribocoupling materials was carried out experimentally on two friction machines UPS-01 and MT-1 (Figure 1) [21], for steel ShKh 15 (an analogue of EU 100Cr6 and US 52100 steels) and steel 45 (analogue of EU C45 and US 1045 steels), RT aviation fuel (a certified analogue of Jet A-1 aviation kerosene), AOH-10 hydraulic aviation oil, MK-8 aviation oil with the addition of oleic acid.

The conducted tribo-kinetic research has established kinetic (N^p, K^p, $N^м$, $K^м$) and energy-activation (E^d, $E^м$) criteria for evaluation of ShKh-15 wear resistance and anti-wear properties of RT and AOH-10, as well as kinetic (N^a, K^a, $N^м$, $K^м$, N^p, K^d) criteria for assessment of the wear resistance of steel 45 and the anti-wear properties of MK-8 with the addition of oleic acid [20,21].

Later, kinetic characteristics (N^d, K^d) were established using the developed tribo-kinetic test procedure as well as energy-activation wear ones (E^d) of ShKh 15 steel in the medium of long-term storable aviation kerosene TS-1 and TS-1* (analogues of Jet A-1 fuel) [20, 22,23], then -kinetic characteristics ($N^м$, $K^м$) and activation energy of the second stage of TR - chemical modification $E^м$ of ShKh 15 in the medium of TS-1 kerosene [23,24,25], as well as kinetic ones (N^d, K^d) and activation energy of TR – surface destruction that is actually the wear E^d [27] of steel 45 during reciprocating motion.
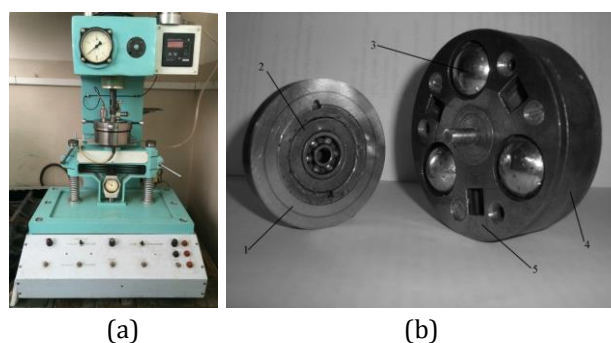

Fig. 1. (a) General view of the UPS-01, (b) A pair of friction, 1-Disc sample, 2-Disc sample holder, 3-Ball, 4- Separator, 5-Pin washer.

Table 1. The Kinetic characteristics and activation energy of surface destruction of E_p of steel ShKh 15 in long-term storage of TS-1 aviation fuel.

Axial load P, N	Temperature T, K^0	Sequential wear reactions	Time intervals Δt, for which it was calculated $\Delta t \times 10^{-3}$, c^{-1}	Value K^P for intervals Δt, $K^P \times 10^{-3}$, c^{-1}	Average values K^P, $K^P \times 10^{-3}$, c^{-1}	The coefficient of estimate variation, K^P, W_K %	Value of wear activation energy, E_p, kJ / mol
98,1	303	1 1	3,6-3 4,2-3,6 4,8-4,2	1,2094 0,9927 1,0595	1,0872	10,2	19,581
	333	1 1	2,4-1,8 3-2,4 3,6-3	1,9868 2,4038 2,1791	2,1899	6,7	

Table 2. The Kinetic characteristics of surface fracture of ShKh 15 steel in medium of TS-1 jet fuel.

Value		Time intervals Δt, for which it was calculated $\Delta t \times 10^{-3}$, c^{-1}	Value K^P for intervals Δt, $K^P \times 10^{-3}$, c^{-1}	Average values K^P, $K^P \times 10^{-3}$, c^{-1}	Trust interval of evaluation $K^P, \pm \Delta K^P \times 10^{-3}$, c^{-1}	Value K^P installed graphically	The variation coefficient of estimation, K^P, W_K %	Value of wear activation energy, E_p, kJ / mol
Axial load P, N	Temperature T, K^0							
9,81	303	2,4-1,8 3,0-2,4 3,6-3,0	0,5334 0,4872 0,4485	0,4897	0,0285	tg240=0,4452	8,6749	19,4219
	333	2,4-1,8 3,0-2,4 3,6-3,0	1,0241 0,8878 1,0305	0,9808	0,0422	tg440=0,9657	8,2176	

Table 3. The energy of activation of two stages of triboreaction for some fuels and lubricants.

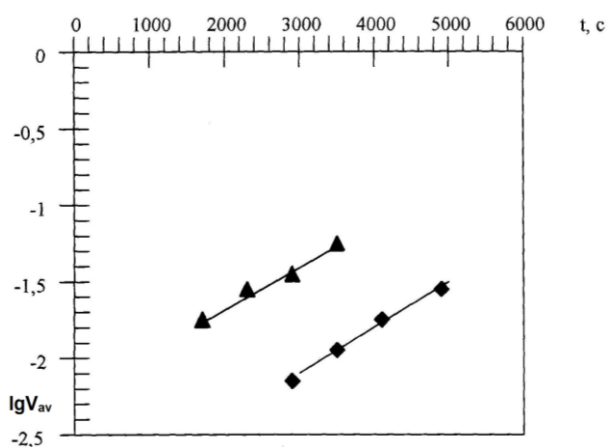| Fuels and lubricants	Construction material	Stage of triboreaction	Energy of activation, kJ / mol	Coefficient of variation W, %	Direction of friction
RT	ShKh 15	Stage 3	21,278	1,9%,	Unidirectional
TS-1	ShKh 15	Stage 2	0,296		
TS-1	ShKh 15	Stage 3	19,421		
AOH-10	ShKh 15	Stage 3	51,76	2,5 %	
TS-1*	ShKh 15	Stage 2	1,98		
TS-1*	ShKh 15	Stage 3	19,58		
Vaseline oil	Steel 45	Stage 3	8,96		Bidirectional

Fig. 2. The average total wear logarithm of three balls lgV$_{av}$ and the duration t for steel ShKh 15 in long-term storage of TS-1 aviation fuel.
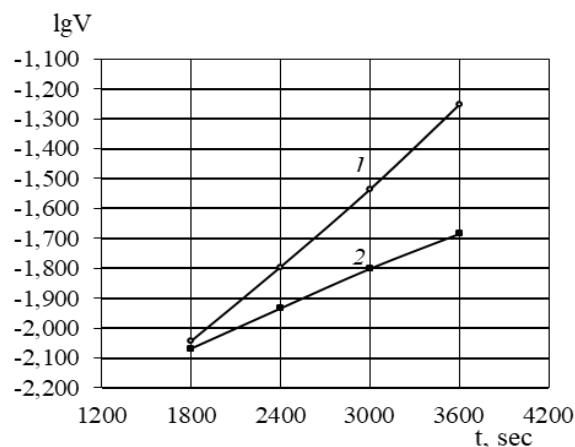

Fig.3 . The average total wear logarithm of three layers and the duration of tribo-kinetic experiments for fuel TS-1 when 1-T = 333 K; and 2- T = 303 K.

According to the results that obtained by the experiment in (Table 1, 2) the (Figure 2) and (Figure 3) were constructed.

With using the proposed methodology for assessing the kinetic characteristics, the values of the activation energy for two stages of triboreaction and a number of lubricants have been obtained in (Table 3).

The universality of the activation energy *E* lies in the fact that this energetic, integral, materials science criterion for assessing three stages of triboreaction is applicable for assessing both the wear resistance of structural materials and wear-resistant fuels and lubricants. This is achieved by studying the materials of triboconjunction: when we change the structural material with a fixed lubricant, then the Eact value characterizes the wear resistance of the structural material under study. And vice versa: by changing lubricants with a fixed structural material, we determine the wear-resistant properties of the lubricants under study. This procedure was performed in the present work.

4. CONCLUSION

1. The possibility of kinetic description of the normal mechanic-chemical wear of the structural elements of tribo-conjugations at boundary lubrication as a general three-stage tribological reaction (triboreaction) has been experimentally confirmed.

2. The experimental calculated method of determination of the kinetic and energy-activation criteria for the evaluation of the wear resistance and compatibility of tribomaterials was experimentally confirmed on the basis of kinetic three-stage triboreaction.

3. The criteria for the evaluation of wear resistance and compatibility of rubbing materials based on the developed methodology for determination of kinetic and energy-activation as well as for evaluation of activation energies of the II and III stages of the triboreaction for determination of the anti-wear properties of long-term storable aircraft fuels TS-1 and TS-1* and also for determination of the activation energy of wear and tear for Steel 45 during reciprocating motion have supplemented the matrix energy-activation criterion for the evaluation of the wear resistance and compatibility of tribo-materials.

4. By to the proposed matrix energy-activation criterion for assessment of the durability and compatibility of triboconjunction materials it is possible to control the durability and compatibility of triboconjunction materials due to the advantage of either one or two stages of tribo reaction.

5. The obtained values (E^d) of anti-wear properties of aircraft long-term storable jet fuels TS-1 and TS-1* and (E^d) of Steel 45 during reciprocating motion can be used to accumulate the bank of energy activation criteria for the evaluation of the durability and compatibility of tribomaterials.

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