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Initiation of a data bank of activation energy values for tribo-reaction wear and modification of Shkh 15 and Steel 45 steels in the environment of hydrocarbon liquids

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Abstract

The kinetic technique, which is developed on the basis of the kinetic three-stage model of normal mechano-chemical wear, is considered. The values of the activation energy of wear of secondary structures of structural steels in the medium of hydrocarbon liquids are obtained by the experimental-calculation method. The obtained results of the assessment of the energy of activation of wear and chemical modification of structural steels in the media of hydrocarbon liquids allow us to establish a data bank of anti-wear and modification properties of secondary structures, which can serve as reference data on the anti-wear and modification properties of secondary structures on structural steels in the media of hydrocarbon liquids.

Keywords: tribokinetic experiment, triboconjugation, activation energy, kinetic model, wear resistance criterion

Introduction

Numerous units of fuel and hydraulic systems of modern technology (pumps, valves, regulators, distributors, etc.) operate in the environment of low molecular weight hydrocarbon liquids, which are at the same time a lubricating medium for the listed units.

Among the tribocoupals of fuel units operating under frictional conditions, the most loaded are the units of high-performance high-pressure fuel pumps, which pump fuel to the consumable tanks of aircraft and storage tanks of low molecular weight hydrocarbon liquids, as well as supply this fuel to the combustion chambers of turbojet and turboprop engines. It is the wear resistance of these components that largely determines the resource and reliability of fuel pumps. The most common are plunger and centrifugal pumps. In plunger pumps, there is a linear contact between the parts of the components that are subjected to friction, namely, the spherical end of the plunger and the inclined washer form a friction pair [1].

The development of scientific and technological progress is impossible without the development of new structural and fuel-lubricants (PMM). To do this, it is necessary to conduct modeling and full-scale (industrial) tests of such materials. These tests require the use of unified, universal, energy, i.e. invariant in known ranges of load values, criteria for assessing the wear resistance of structural materials and anti-wear properties of fuel and lubricants [2].

Analysis of research and publications

Recently, the number of scientific and experimental works on the use of fracture activation energy, including surface (i.e. wear) to explain the destructive processes of structural materials, mainly steels, in the fuel and lubricants environment has increased [3]. The use of activation energy is also present in the dissertation [4], where its value is determined by the cohesive properties of matter.

In the structural-energetic theory of friction and wear and the theory of structural adaptability of tricoupling materials, the following characteristics are used: specific fracture work – A_D, energy intensity of the friction system by thermal index – "ECTq", critical value of friction work – A_{cv}, critical (limiting) density of internal energy – U^*, (for abrasive wear), surface energy or surface tension – γ, the work of the WOE electron output, exo-electron emission – EEE, contact potential difference – U_{CPD} [5, 6, 7]. At the same time, the energy characteristics of wear resistance characterize the processes of surface failure, reasonably assess the friction conditions, the choice of tricoupling materials, their coupling within normal wear (without damage) determine the boundaries of the transition to damage.

Thus, the most common, best studied and experimentally tested criterion is the specific work of surface fracture (the ratio of the work of friction force to the amount of wear) is an imaginary characteristic of wear resistance and depends not only on the surface strength of the material, but also on the ability of the tribosystem to dissipate energy. Use of surface energy γ complicated by the lack of reliable data on the value γ of pure metals, not to mention alloys in real conditions.

The energy criterion for assessing compatibility – surface energy or surface tension γ, electron output work, etc., as well as wear resistance criteria, are not direct compatibility characteristics. In addition, there are no reliable data γ even for pure metals, the values γ and electron yield are different for different faces of the crystal.

The most direct, quantitative, structural-energetic (materials science), kinetic (physicochemical) characteristic useful for assessing the wear resistance of triboconjugation materials is the activation energy of surface destruction (wear) E^D, which characterizes a potential barrier to the implementation of elementary acts of destruction. At the same time, in the range of structural adaptability of triboconjugation materials, E^D must be invariant, which can be used as a criterion assessment of anti-wear properties of lubricants. This, in contrast to the existing variety of criteria for assessing wear resistance, regulated by GOST 9490-75 and GOST 23.002-78, allows the use of E^D as a universal, the only criterion for assessing the tribological properties of triboconjugation materials [8].

The universality of E^D is confirmed by its use as a criterion for evaluating various physical processes. For example, the use of activation energy U as a function of resistance to deformation of a plastically deformable metal sample is known. In this case, U, which describes the processes of rearrangement of atoms in the crystal lattice, is determined by the degree of violation of the order caused by the deformation. Despite the good singing of the fall in U values with the activation energy of diffusion and self-diffusion, as well as the confirmation of the equality of $U \cong 20RT_{mp}$. (T_{mp} is the melting point), this conclusion does not inspire much confidence due to the low accuracy of estimating the degree of violation of the order of the crystal lattice [8].

However, even the correct choice of the criterion for evaluating the wear resistance and compatibility of triboconjugation materials does not guarantee the correct determination of the wear resistance and compatibility of these materials. The correct choice of the criterion for assessing wear resistance and compatibility is a necessary condition, but not sufficient. A sufficient condition for the correct assessment of wear resistance and compatibility of triconjugation materials is the correct methodology for assessing the wear resistance and compatibility of these materials.

To date, there are three methods for estimating the activation energy: 1) graphical; 2) extrapolation; 3) kinetic. In the first methodology, the value of E^D depends on the scale of the coordinate system. Therefore, E^D can only be used in comparative tests. In the second methodology, the value of E^D depends on the subjective qualities of the researcher (tester), since extrapolation is an approximate determination of the values of $f(x)$ at points x that lie outside the segment (x_0, x_n) by their values at points x_o<x<... <x_n. However, the best, i.e. the most accurate, technique is the third, kinetic, where the value *of* E^D is determined by the laws and equations of chemical kinetics, when the order of a chemical reaction is first determined, then the rate constant of this reaction is at least two temperatures, and according to the Arrhenius equation, E^D is calculated [8].

Research methodology

Next, we will consider the kinetic technique, which is developed on the basis of a kinetic, three-stage model of normal mechano-chemical wear, for the description of which the following scheme of the tribological reaction (TR) is used:

$$RB \overset{\text{A}}{\leftrightarrow} Me_{x_1}(RB)^*_{y_1} \overset{\text{M}}{\rightarrow} Me_{x_2}(RB)^*_{y_2} \overset{D}{\rightarrow} Me_{x_3}(RB)^*_{y_3} \overset{D}{\rightarrow} Me^0, \quad (1)$$

where RB is the lubricant involved in triborecia: in the simpler case, only the effect of the active component of the lubricant – the additive, R – the hydrocarbon radical of the additive, B – the active component of the additive, Me^o – the juvenile areas of the surfaces of the contacting materials of triboconjugation; x_i, y_i is the fractional coefficient of components that are analogues of stoichiometric coefficients in a true chemical reaction.

An asterisk indicates active triboreaction complexes:

$Me_{x_1}(RB)^*_{y_1}$ – adsorption complex formed as a result of adsorption of lubricant (RB) on juvenile areas of surfaces of structural materials triboconjugations (Me^o). This complex is active in relation to the next stage – chemical modification (M);

$Me_{x_2}(RB)^*_{y_2}$– modified (dissipative secondary) structures active in relation to the stage of surface destruction (D);

$Me_{x_3}(RB)^*_{y_3}$ is a complex of surface destruction (wear products), in fact, a product of a tribological reaction.

As can be seen from equation (1), only the first stage - adsorption (A) is accepted as reverse, i.e. bilateral. The rest of the stages are considered to be significantly reversed, i.e. unilateral. Juvenile sections of contacting structural materials are both the initial reaction component and the catalyst of triborereaction, which accelerates the course of the first stage A. At the same time, the total area of juvenile areas, i.e. the concentration of Me^o at normal (stationary) wear remains constant, while the amount of starting materials is constantly decreasing due to wear. The amount of lubricants and structural materials is assumed to be large enough and their concentration does not depend on the duration of triboreaction. Otherwise, it is necessary to use absolute values, not concentrations.

According to the given kinetic three-stage model of normal mechano-chemical wear, an experimental and computational method for assessing the kinetic characteristics and activation energies of all three stages of triboreaction was developed. According to which, we first determine the kinetic characteristics and activation energy - the E^D of the third, last stage of triboreaction, that is, in fact, wear, since as a result of tribokinetic tests of triboconjugation materials.

We measure the diameters of the wear spots of the three balls and calculate the wear volumes, i.e. the volumes of the ball segments V_w. After conducting similar tribokinetic tests at 4-5 values of the duration of such tests (t), we plot the dependence of $\lg V_w$ on the duration of the tests t. Straight lines of such graphs indicate the first order of the stage under study (in this case, the third stage of the triboreaction), i.e. $N^D \cong 1$, and the tangent of the angle of inclination of the lines to the abscissa axis graphically determines the velocity constants of the stage under study, in this case K^D. But the graphical assessment and value of the order and rate constants of the studied stages of triborereaction is approximate. Therefore, more accurate values of these kinetic characteristics must be established analytically, that is, determined by the appropriate formulas.

$$N^D = \frac{\lg W_2/W_1}{\lg V_w t_{i+1}/V_w t_i},$$

where W_1 and W_2 are the rates of stage III, i.e. wear, which are determined for the intervals of duration of tribokinetic tests:

$$\Delta t = t_{i+1} - t_i.$$

That is,

$$W_1 = \frac{V_w t_{i+1} - V_w t_i}{\Delta t},$$

where $V_w t_{i+1}$ and $V_w t_i$ are the wear volumes of the three balls during the duration of tribokinetic tests at the duration t_{i+1} and t_i, respectively.

In this case, the order of the third stage can be calculated in two ways: 1) for each interval Δt, and then calculate the arithmetic mean of N_i; 2) for the initial and final intervals Δt, that is, N^D is calculated during the entire duration of tribokinetic tests.

The rate constant of the III stage, i.e. wear, was calculated using the difference V_w in the interval Δt, according to the equation:

$$K^D = \frac{\Delta V_w}{\Delta t V_{w.m}} = \frac{W}{V_{w.m}}$$

where $V_{w.m}$ is the arithmetic mean of V at the beginning and end of the interval Δt.

Having established at least 4 values *of* K^D, it is possible to carry out statistical processing of the results obtained, i.e. to calculate the average values *of* K^D, the confidence interval of the estimate *of* K^D – ΔK^D, and the coefficient of variation of the assessment of the specified estimate – Z_c.

Repeating the tribokinetic tests according to the above method at a temperature other than T_1, according to the Arrhenius equation, we calculate the activation energy of the III stage of TR - the actual wear of triboconjugation materials.

In addition, the formula proposed by the author for calculating the area of secondary structures participating in the TR (S_{ss}.) [8] and, as a result, the calculation of the relative area of secondary structures:

$$\delta = \frac{S_{ss}}{S_к}$$

where S_k is the contact area, i.e. the area of three contact spots, made it possible to calculate the kinetic (N^m, K^m) characteristics and activation energy of the second stage of TR-chemical modification (E^m):

$$S_{\text{вс}} = S_{\text{к}} - \frac{\Delta V_{w.m}}{\Delta t h_{ss} K^D}$$

where $\Delta V_{w.m} = V_{wti+1} - V_{wti}$ is the wear volume of three bullets in the interval $\Delta t = t_{i+1} - t_i$, respectively; h_{ss} is the thickness of secondary structures or the thickness of chemical modification, the value is variable: with an increase in the duration of tribokinetic tests, h_{ss} decreases.

The kinetic characteristics of the first stage of TR (N^a, K^a) and the activation energy can be determined by conducting tribokinetic tests according to the specified algorithm with a lubricant with a chemically active substance, i.e. an additive, for example, oleic acid [2], which allows determining the specified kinetic parameters and activation energy of tribosorption for the operation of a chemically active substance.

These tribokinetic tests were performed at one fixed temperature T_1. If we conduct similar tribokinetic tests at a temperature other than T_1 T_2, we get the values of similar kinetic criteria N and K of the three stages of TR. And knowing K at two temperatures (T_1 and T_2) we calculate the activation energies of these stages according to the Arrhenius equation:

$$E = \frac{RT_1T_2}{T_1 - T_2} \ln\frac{K_2}{K_1} = \frac{1{,}9144 T_1T_2}{T_2 - T_2} \lg\frac{K_2}{K_1} \cdot 10^2$$

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 $R = (8.3143 \pm 0.0012) \cdot 10^3$ J/K·mol times the modulus of conversion of natural logarithms into decimals, which is equal to 2.3056.

The proposed method for conducting tribokinetic tests of triboconjugation materials was tested experimentally. On the friction machine "UPS-01" (Fig. 1, 2 and 3), which is a modernized, i.e. improved, analogue of the friction machine “КИИГА-2”, Steel 45 was studied, in the environments of aviation fuel RT, aviation oil hydraulic oil AMG-10, aviation oil MK-8 with the addition of oleic acid [2]. The “КИИГА-2” friction machine was used to determine the wear resistance of ShKh 15 in the long-term storage environments of TS-1 and TS-1* aviation fuels [8-11]. In addition, tribological tests of Steel 45 steel were carried out in the environment of inactive vaseline oil on the ATKD friction machine (modernized MT-1 friction machine) in the reciprocating mode [12].

Fig.1. Appearance of the device UPS -01

Research results.

The conducted tribokinetic tests established kinetic (N^D, K^D, N^m, K^m) and energy-activation (E^D, E^m) criteria for assessing the wear resistance of ShKh 15 and anti-wear properties of RT and AMG-10, as well as kinetic (N^a, K^a, N^m, K^m, N^D, K^D) criteria for assessing the wear resistance of Steel 45 and the anti-wear properties of MK-8 with the addition of oleic acid [2]. Later, using the developed method of tribokinetic tests, kinetic (N^D, K^D) and activation energies of wear ShKh 15 (E^D) were established in the aviation fuel media "TS-1" and "TS-1*" of long-term storage [8, 9], kinetic (N^m, K^m) and activation energy of the II stage of TR - chemical modification (E^m) SHX-15 in the medium "TS-1" [10, 11], as well as the kinetic (N^D, K^D) and activation energy of TR - surface destruction, i.e., actually wear (E^D) [12] Steel 45 during reciprocating motion.

The values of the activation energy of the wear of secondary structures on the ShKh 15 in the aviation fuel environment for RT turbojet engines and in the aviation lubricant environment for AMG-10 hydraulic systems with the reproducibility of the results characterized by a coefficient of variation of not more than 2.5 % were established [2].

All results are shown in Table 1. E^D, E^m. According to the results of tribological tests of Steel 45 steel in the medium of inactive vaseline oil on the ATKD friction machine in the reciprocating motion mode, kinetic characteristics (reaction rates, order and velocity constants) and shear activation energy E^D =8.96 kJ/mol were determined, which is significantly less than in unidirectional motion [12].

Table 1.

Research results

	Name of the PMM	Meaning E^D kJ/mol	Meaning E^m kJ/mol
1	AMG-10 oil	51,76	1,14
2	Fuel RT	21,28	9,39
3	Fuel TS-1	20,31	0,296
4	Fuel TS-1* for long-term storage	19,58	1,98

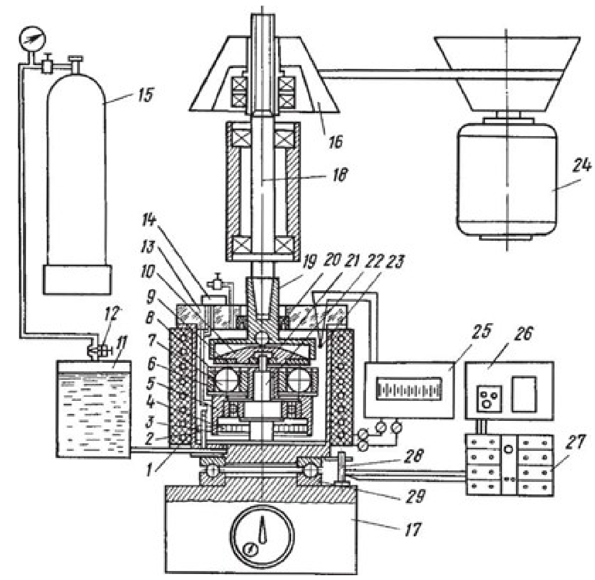

Fig. 2.- Scheme of the UPS -01 device: 1 - electric spiral; 2 - fuel chamber; 3 - limiter; 4 - spiral spring; 5 - movable block; 6 - separator; 7 - sample ball; 8 - pressure washer; 9 - sample disk; 10 - sample disk holder; 11 - fuel tank; 12-throttle valve; 13-fuel chamber cover; 14-limit switch; 15-nitrogen cylinder; 16 - flat disk drive pulley; 17 - arrow indicator; 18 - drive shaft; 19-adapter; 20 - sealing collar; 21-spherical bearing; 22 - central axis; 23-thermocouple; 24-electric motor; 25-thermoregulator KMP1-502; 26-automatic unit; 27-amplifier; 28-tension beam; 29-bearing

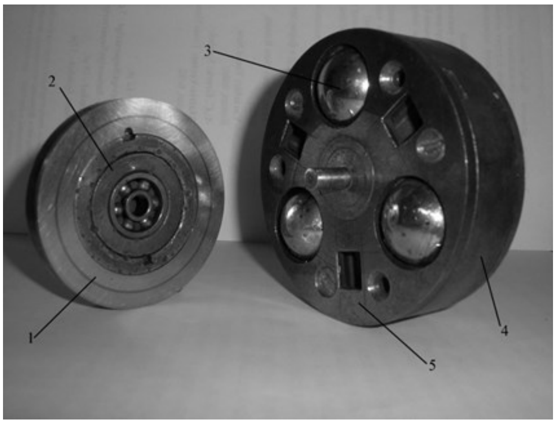

Fig. 3. Friction pair of friction machines UPS -01 and “КИИГА-2”: 1-disk-sample; 2-disk-sample holder;

3-ball; 4-separator; 5-thrust washer

Conclusions

1. The obtained results of the assessment of the energy of activation of wear E^D and chemical modification of ShKh 15 steel in the oil (Table 1) allow us to establish a data bank of anti-wear and modification properties of ShKh 15 steel, which can serve as reference data on anti-wear and modification properties of ShKh 15 steel in the environments above the specified hydrocarbon liquids E^m.

2. To obtain secondary structures steel ShKh 15 with better anti-wear properties, it is necessary to spend more energy for the activation of chemical modification, with the exception of TS-1* fuel for long-term storage E^m

3. An exception to this rule can be preliminarily explained by changes in the physicochemical composition of TS- 1 fuel* in comparison with the similar composition of TS-1 according to ДСТУ 320.001249943.011-99, which indicates the influence of the physicochemical composition of fuel and lubricants on energy costs when modifying the aircraft on ShKh 15 steel in the environments above the specified fuel and lubricants.

4. For a more accurate explanation of this phenomenon, it is necessary to conduct additional studies to establish the reasons for the increase for less wear-resistant aircraft on ShKh 15 steel in the TS-1 fuel environment* E^m

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Богданович О. І., Пузік С. О., Токарук В. В., Хімко А.М. Започаткування банка даних значень енергії активації трибореакції зносу та модифікування сталей ШХ15 та Ст 45 в середовищі вуглеводневих рідин

Розглянуто кінетичну методику, яка розроблена на основі кінетичної трьох стадійної моделі нормального механо-хімічного зносу. Представлені значення енергії активації зносу вторинних структур конструкційних сталей в середовищі вуглеводневих рідин отримані експериментально-розрахунковим методом. Отримані результати оцінки енергії активації зносу та хімічного модифікування конструкційних сталей в середовищах вуглеводневих рідин дозволяють започаткувати банк даних протизносних та модифікаційних властивостей вторинних структур, що може слугувати довідковими даними по протизносним та модифікаційним властивостям вторинних структур на конструкційних сталях в середовищах вуглеводневих рідин.

Ключові слова: трибокінетичний експеримент, трибоспряження, енергія активації, кінетична модель, критерій зносостійкості