

Electrodynamics of frictional interaction in tribolink “metal-polymer”

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Abstract. The materials of the article illustrate the estimation of the energy loading of a metal friction element in the metal-electrolyte-polymer friction pair while forming various types of double electrical layers with the release of its thermal stabilization state. The energy loading of the contact spots of the microprotrusions of the friction pairs of braking devices depends to a large extent on the electrical, thermal and chemical fields that are of a different nature to an allowable temperature and are above the surface layers of the polymer patch. The latter is significantly influenced by double electrical layers that are formed at the boundaries of the phases "metal-metal", "metal-polymer", "metal-semiconductor", "semiconductor-semiconductor" and "metal-electrolyte". When two electrically conducting phases come into contact with electrothermomechanical friction, a difference in electrical potentials arises, which is due to the formation of a double electric layer, that is an asymmetric distribution of charged particles near the phase boundary. The structure of the double electric layer does not matter for the magnitude of the reversible electrode potential, which is determined by the variation of the isobaric-isothermal potential of the corresponding electrochemical reaction.

1. Introduction

The energy loading of the contact spots of the microprotrusions of the friction pairs of braking devices depends to a large extent on the electrical, thermal and chemical fields that are of a different nature to an allowable temperature and are above the surface layers of the polymer patch. The latter is significantly influenced by double electrical layers that are formed at the boundaries of the phases "metal-metal", "metal-polymer", "metal-semiconductor", "semiconductor-semiconductor" and "metal-electrolyte".

Due to electromechanical friction interaction, an electrical double layer in friction pairs effects the formation of the microthermo-battery, which works in the micro-thermoelectro-generator and microthermoelectro-refrigerator modes. The generated current in the chain by triboEDS is an algebraic sum of the following components:

$$I_a = I_{ck} + I_V + I_L + I_N + I_H,$$

where I – currents, raised as a result of: electrification of slide and contact; movement of charged particles of friction mass transfer; a sorption-desorption process at the surface layers of the contact;



thermal backward charge, formed during the destruction of friction contact (current impulse). However, the following points were not studied fully in this work:

- Forming of double electric layers of similar charges ("ion-ion" and "electron-electron").
- The metal potential is compared to electrolyte, which consists of a thick and diffused part of the double electrical layer.
- Specific adsorption of an ion on the metal surface.
- Change of the potential in a friction pair "metal – electrolyte" and arising density of the current.
- Part of the potential change in the friction pair "metal-electrolyte", which effects the thermostabilized state of the metal friction part.

2. Materials and methods, physical models

2.1 Statement of the task and purpose of the work

In this publication, the following questions are considered in relation to the problem:

- the nature of the appearance of a double electric layer in electrothermomechanical friction;
- the structure of a double electric layer at the boundary of the "metal-electrolyte" phases in the electrothermomechanical frictional interaction of friction pairs;
- classical approach and approach from the standpoint of electrothermomechanical friction, to the potential change in the friction pair (the "metal-electrolyte" phase) of the friction assemblies and its effect on the thermal stabilization state of the metallic element.

The aim of the work is to develop an in-depth approach to the evaluation of the thermostabilization state of a metal friction element in a friction pair "metal-electrolyte-overlay" due to the formation of various types of double electrical layers during their electrothermomechanical interaction.

As the materials of the metal-polymer friction pair, 35KhNL-FK-24A steel is considered to be used in belt-block brakes of drilling winches.

The studies presented in the materials of the first and second part of the articles were carried out on the basis of the method of nonequilibrium tribology.

2.2 The nature of the appearance of a double electric layer in electromechanical friction.

When two electrically conducting phases come into contact with electrothermomechanical friction, a difference in electrical potentials arises, which is associated with the formation of a double electric layer, i.e., an asymmetric distribution of charged particles near the interface. The last ones are in the friction pairs of braking devices "metal-vacuum" (a), "metal (1) - metal (2)" (b), "metal-polymer" (c), "metal-own semiconductor" (d), "metal-semiconductor with an admixture" (e), "intrinsic semiconductor-semiconductor with an admixture" (f), "metal-electrolyte" (g); "washing environment - metal", "metal - polymer - electrolyte - polymer" (h) [see Fig. 1].

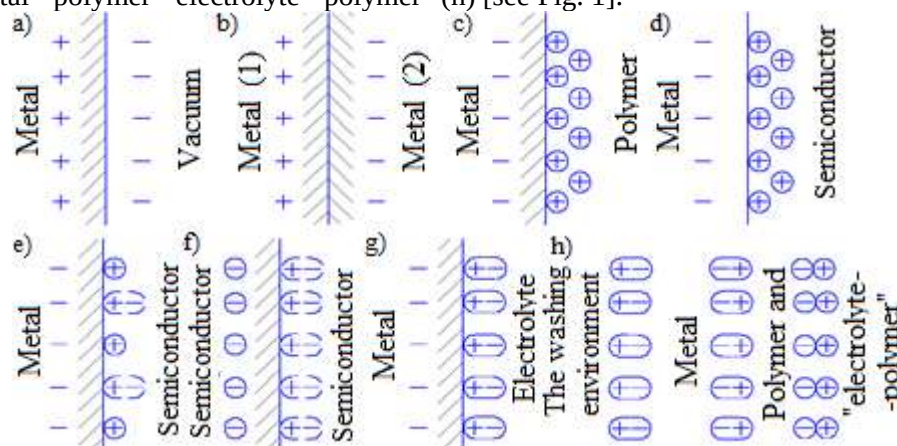


Figure 1. The scheme of the structure of a double electric layer in the friction elements of brake devices within two or more phases: *a* is the emission of electrons from a metal into a vacuum; *b*-contact potential of the second kind (electron work function); transition of electrons from one metal to

another; c - contact potential in a pair of friction; d, e - the contact potential in a friction couple with a proper semiconductor and with impurities; f is the contact potential arising between the intrinsic and semiconductor impurities; g - the contact potential of the Volta; transition of cations from metal to electrolyte or from electrolyte to metal; h - contact potential in friction pairs as in a multilayered object.

The scheme in Fig. 1 g is of great interest.

Let us consider the act of friction pair interaction between a "metal-polymer" in the presence of an electrically conductive liquid formed in connection with the burn-out of the binding components of their surface layers of a polymer patch. The participation of the electrolyte as a slotted capillary layer leads to the formation of potential jumps at the "metal-electrolyte" boundaries (Fig. 2). A more complicated scheme is shown in Fig. 1 h . According to the last name of the scheme "multilayered object". It includes a "washing environment" interacting with the outer surface of the heated metallic friction element, thereby creating a first double electrical layer. The frictional interaction of the inner (working) surface of the metal element with the outer surface of the polymer patch (up to the permissible burn-up temperature of the bonding components in its surface layers) contributes to the appearance of a second double electric layer (also referred to in Fig.1). The third double electric layer occurs when the surface temperature becomes higher than permissible and the frictional interaction of the metal-electrolyte-polymer friction pair occurs, since the electrolyte occupies a small area (islets) on the working surface of the lining. In future, some of the schemes of the structure of the double electric layer in friction elements of brake devices that are of practical interest will be considered.

2.3 The structure of a double electric layer at the "metal-electrolyte" boundary with the electrothermomechanical frictional interaction of friction pairs and its mathematical description.

The structure of the double electric layer does not matter for the magnitude of the reversible electrode potential, which is determined by the variation of the isobaric-isothermal potential of the corresponding electrochemical reaction. At the same time, the structure of the double electric layer plays an important role in the kinetics of electrical processes, including in the kinetics of ion exchange under equilibrium conditions, characterizing the intensity of this exchange (the value of the exchange current, i), and as a consequence, in the occurrence of the thermal stabilization state of the metallic friction element.

According to G. Gelmgolts, the double electric layer is likened to a plane capacitor, one of its plates coinciding with the plane passing through surface charges in the metal, and the other - with a plane connecting the centers of gravity of the charges of ions in the electrolyte, but attracted by electrostatic forces to the metal surface (Figure 3a).

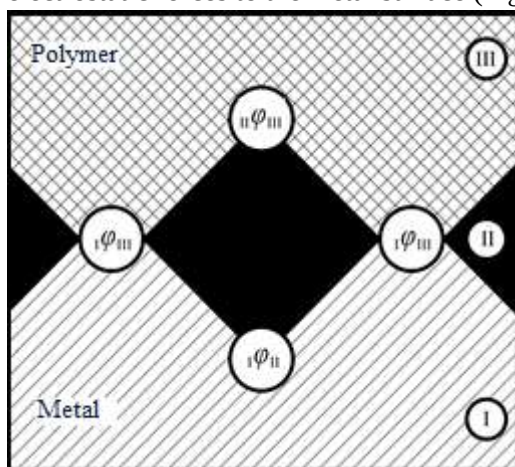


Figure 2. The slit capillary layer from the electrolyte on the phase boundaries "metal (I) - electrolyte (II) - polymer (III)" (physical model)

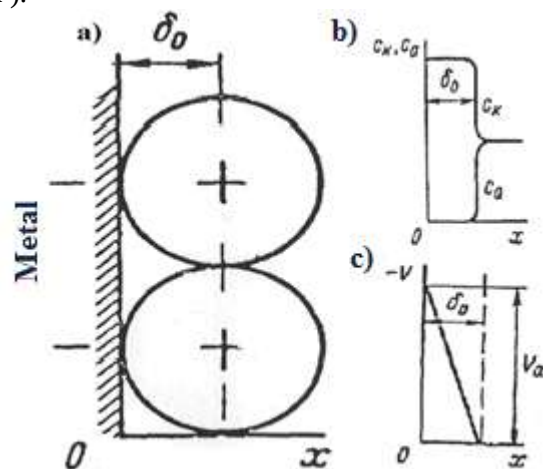


Figure 3. The dense structure of the double electric layer, represented in the form of a flat capacitor (a) and constituting changes in the concentration of ions (b) and the metal potential (c)

The thickness of the double electric layer, δ_0 (that is, the distance between the capacitor stacks), is taken to be equal to the radius of the hydrated ion, $\delta_0 = r_{\text{Hg}}$, i.e. of the order of several angstroms [2]. According to the law of electroneutrality, which is valid for the interface, the surface charges of metal q_{Me} must be compensated by charges q_p , attracted to the metal surface by ions from the electrolyte:

$$q_{\text{Me}} = -q_p, \quad (1)$$

where q_{Me} and q_p - specific surface charges (or charge densities) from the side of metal and electrolyte.

The charge density of a flat capacitor is directly proportional to the jump in potential V_a due to the ionic double electric layer,

$$q_{\text{Me}} = CV_a, \quad (2)$$

C – double layer volume; V_a - the potential directly at the metal surface, referred to the potential in the middle of the electrolyte (conditionally assumed to be zero), which varies linearly within the dense part of the double layer (Fig. 3c). The capacitance of a flat capacitor is determined from the dependence of the form:

$$C = \frac{q_{\text{Me}}}{V_a} = \frac{D}{4\pi\delta_0 \cdot 9 \cdot 10^5} \text{ mF/cm}^2, \quad (3)$$

D - the dielectric constant of the medium filling the space between the plates of the capacitor; in one case, it is an electrolyte, and in another - products of wear of polymer linings, which are charged negatively.

Due to the thermal motion of the molecules of the electrolyte and ions, as a result of electrothermomechanical friction, and also the mutual repulsion of ions with the same charge, some ions leave their fixed position at the surface of the metal, according to O. Stern, and is distributed in the electrolyte relative to its surface along the Guy's, diffusely with which decreases as the volume density of the charge is removed from it [3] (Fig. 4a).

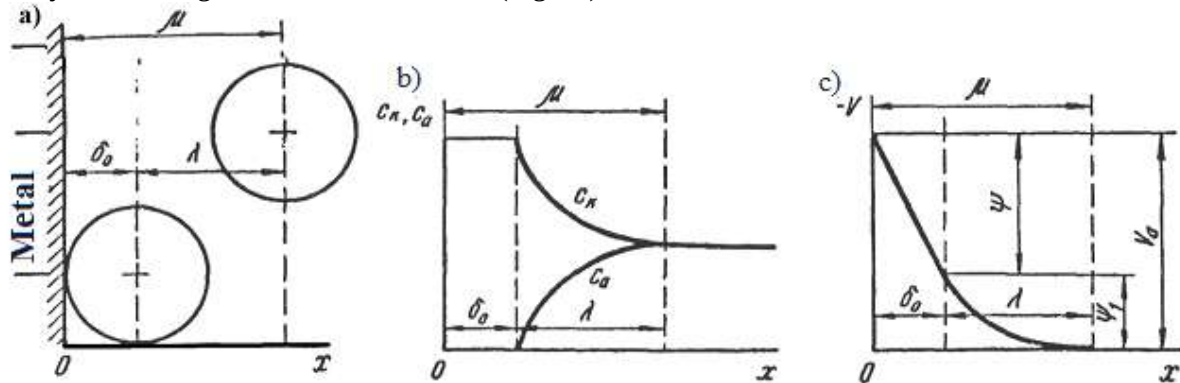


Figure 4. The diffusion structure of a double electric layer with a decreasing bulk density of charge (a), and components of the change in the concentration of ions (b) and the metal potential (c)

The thickness of this diffuse part of the double electric layer λ is equal to the data of A.N. Frumkin: in pure water, up to 1 μm , for not very low concentrations of electrolyte - in $10^{-7} - 10^{-6}$ cm, and in concentrated electrolytes - in tens or units of angstroms.

Thus, the potential of the metal relative to electrolyte V_a consists of two components: ψ and ψ_1 , which, respectively, fall on the dense and diffuse part of the double layer with thickness δ_0 and λ (Fig. 4c), i.e.:

$$V_a = \psi + \psi_1. \quad (4)$$

Figures 3b and 3c show the ion density changes (c_a , c_k) corresponding to these models of the ionic double electric layer with distance x from the surface of the metal.

For strong electrolytes, without a significant error, let us take $\lambda \approx 0$.

Theoretical studies of P.J. Debye and E.A. A.J. Gückel made it possible to obtain the following for a double electric layer:

$$q_{Me} = C(V_a - \psi_1) = -\sqrt{\frac{DRT}{2\pi}} \sqrt{\sum_i \left[\exp\left(-\frac{n_i F \psi_1}{RT}\right) - 1 \right] c_i}, \quad (5)$$

n_i and c_i - valence and concentration of ions of the variety i ; R - gas constant; T - temperature at the metal-electrolyte interface; $(\Phi_+ + \psi_1 n_k = F)$ and $(\Phi_- - \psi_1 n_a = F)$ - the total value of the change in the potential energy during adsorption for cations and anions, taking into account the effect of the electric field; Φ_+ and Φ_- - the value of the adsorption potentials for cations and anions, respectively, independent of the electric field (the values of the change in the potential energy during the transfer of 1 mole of material from the middle of the electrolyte to the surface at $\psi_1 = 0$) [4].

Later, O. Stern suggested taking into account the specific adsorption of ions on the metal surface. Therefore, in electrolytes containing surface active ions, their number in the dense (Helmholtz) part of the double layer may not be equivalent to the charge of the surface of the metal, but exceed it by some amount depending on the properties of the ions and the charge of the metal:

$$q_{Me} = C(V_a - \psi_1) = -(q_{i1} + q_{i2}); \quad (6)$$

for a monovalent electrolyte [4]:

$$q_{i1} = 2Fc\delta_0 \left[\exp\left(-\frac{\Phi_+ + \psi_1 F}{RT}\right) - \exp\left(-\frac{\Phi_- - \psi_1 F}{RT}\right) \right]; \quad (7)$$

$$q_{i2} = +\sqrt{\frac{DRTc}{2\pi}} \left[\exp\left(-\frac{\psi_1}{2RT}\right) - \exp\left(\frac{\psi_1 F}{2RT}\right) \right]. \quad (8)$$

Further development of the theory of the structure of a double electric layer was given in the papers of A. N. Frumkin and his school, T. Graham, et al. According to T. Graham, in the planar (Helmholtz) part of the double layer, there is an internal plane of the electrical centers of specifically adsorbed ions (Only anions), which can approach closer distances δ_{adc} , with the potential corresponding to this plane ψ_{adc} (Fig. 5).

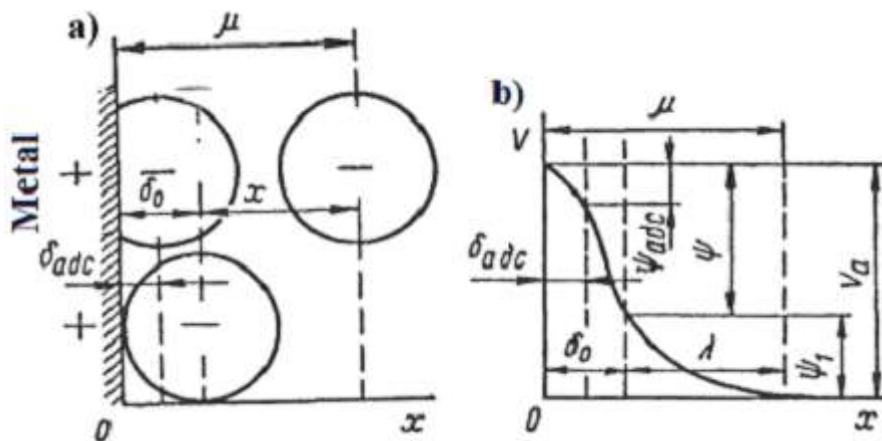


Figure 5. The structure of the double electric layer (a) for the specific adsorption of anions (b) For thermodynamic equilibrium, the total potential jump at the "metal-electrolyte" boundary, i.e., V_a , is interesting, as well as the remaining jumps of potentials whose algebraic sum is equal to the reversible e.m.f. with. chains of the E_{obp} .

Many electrochemical processes take place on electrodes with irreversible (nonequilibrium) potentials, for which it is necessary to pass charged particles (ions) through a double electric layer. In this case, the ions are affected by the electric field of the double layer with its gradient in flat part ψ/δ_0 , which depends on the structure of this layer and changes the activation energy of the electrochemical process. Thus, in the kinetics of electrochemical processes, it is necessary to take into account the structure of the double electric layer.

2.4 The classical approach to the jump in the potential in a pair of friction (the "metal-electrolyte" phase) of friction assemblies and its effect on the thermal stabilization state of a metallic element.

The mechanism for the appearance of a jump in the potential at the metal-electrolyte interface due to the oxidation and reduction of the metal itself, which is the working surface of the friction element on the surface of the polymer patch (see Figure 1g) can be represented as follows. Cations on the working surface of the metal friction element have an average supply of potential energy corresponding to point 1 in Fig. 6. Moving the cation to the left in the energy field, that is, pressing it into the metal of the working surface of friction or coming closer to the neighboring cations of its crystal lattice, requires a lot of work to overcome repulsive forces, which is expressed by upward energy curve 1 - 1'. Moving the cation to the right, i.e. its detachment from the working surface of the friction element in electrothermomechanical friction with the transition to vacuum, requires much work (curve 1 - 1'') of corresponding evaporation energy U_e , second temperature below the allowable materials for the polymer lining the process virtually does not take place.

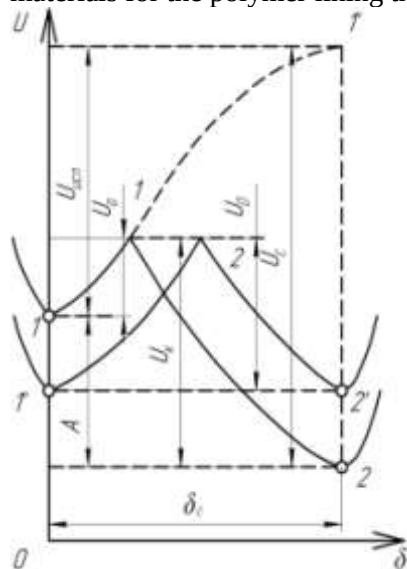


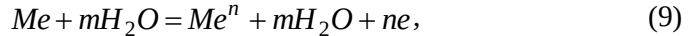
Figure 6. Scheme of energy change during evaporation of metal cation in vacuum and during transition to electrolyte during electrothermomechanical frictional interaction of friction pairs: 1 - moment of contact of metal with electrolyte; 2 - moment of establishment of equilibrium in tribo-conjugation

The polar molecules of the electrolyte-solvent (as an example, water), respectively, orienting themselves to the surface metal cations (Figure 6), facilitate the transition of cations to the electrolyte with the release of solvation energy, since the level of the solvated ion is lower than the cation in vacuum by the amount of U_c , so that the energy of the cations in the electrolyte at nearest possible distance δ_0 from the working surface of the metallic friction element corresponds to point 2 in Fig. 6. The energy curves of the solvated ion rising to the left and to the right correspond, respectively, to the detachment of the cation from the solvating electrolyte molecules and the approach of the cation to the molecules of the electrolyte at distances less than in the spontaneously formed solvate complex.

In order to pass into the electrolyte, the surface metal cation must overcome only the energy barrier (Figure 6. curve 1'-2), with $U_a \ll U_c$, i.e. this process is more probable. The difference in the levels of potential energies at points 1 and 2, equal to A, corresponds to the work of the process of the transition of the first metal ion to the electrolyte. To transit from the electrolyte to the metal, the solvated cation in the electrolyte must overcome energy barrier U_k (Figure 6, curve 2-1), with $U_k > U_a$, i.e. this process (cathodic) is less likely than the first (anodic).

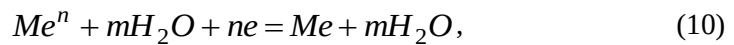
Thus, if in the interaction of a metal with an electrolyte, the phase boundary is crossed only by metal ions, then, according to the investigations of A. N. Frumkin and his school, two conjugate processes occur:

- transition of these ions from the metal into the electrolyte with the formation of solvated ions (oxidation or anodic process):



where Me – metal; m - number of metal atoms in the oxide molecule; ne - the number of ions and electrons formed; the rate of this process, measured by the number of ions passing from phase to phase through unit surface area of the frictional interaction per unit time, is expressed in terms of the emerging current density $\vec{i}$;

- discharge of these ions from the electrolyte with their isolation on the surface of the metal in the form of neutral atoms forming part of the crystal lattice of the metal (reduction or cathodic process):



whose velocity can also be expressed in terms of corresponding current density $\vec{i}$.

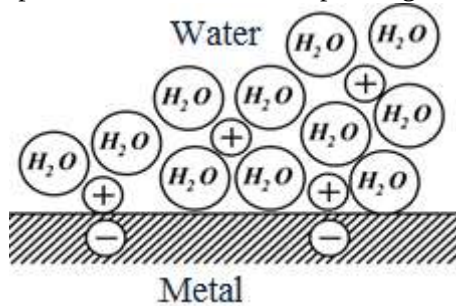


Figure 7. The model of the boundary layer "metal-electrolyte" in the event of a jump in the potential at this boundary.

Which of these processes predominates in electrothermomechanical friction is determined by the level of the potential energy of the cations at the sites of the crystal lattice of metal U_1 and in electrolyte U_2 . If $U_1 > U_2$, then $\vec{i} > \vec{i}$, i.e., the anodic process predominates - the transition of metal ions to the electrolyte (see Figure 7), the total velocity of which is:

$$i_a = \vec{i} - \vec{i}, \quad (11)$$

if $U_2 > U_1$, then $\vec{i} > \vec{i}$, i.e., the cathodic process prevails, while the discharge of metal ions occurs from the electrolyte, the total velocity of which is equal to:

$$i_k = \vec{i} - \vec{i}. \quad (12)$$

When $U_1 > U_2$ (see Figure 6), the transition of some cations to the electrolyte is accompanied by a decrease in the average potential energy of the surface cations (point 1 moves downward), the appearance of excess negative charges on the metallic surface and an increase in energy barrier U_a . Increase in the concentration of ions at the metal surface is accompanied by an increase in the reserve of their energy (point 2 moves upward), the acquisition of an excess positive charge by the electrolyte, and a decrease in energy barrier U_k . Thus, the resulting double electric layer hinders the flow of the direct process and facilitates the reverse process.

When the energy level of the ions on the surface of the metal and in the electrolyte becomes the same, that is, $U'_1 = U'_2$ (which usually occurs quite rapidly), a dynamic equilibrium is established at which $U_a = U_k = U_0$ and the velocities of the anodic and cathodic processes are:

$$\vec{i} = \vec{i} = i_0, \quad (13)$$

where i_0 - the exchange current density due to the constantly flowing exchange of ions between the metal and the electrolyte.

When equilibrium is reached, the change in the mass of the metal is $\Delta m = 0$, i.e., dissolution of the working surface of the metallic friction element does not occur.

In the second part of the article materials, it is shown in what way the braking state of the metallic friction element is achieved in the temperature zone higher than the allowable for the surface layer of the polymer patch.

3. Results and discussion

One of the most important aspects of the influence of electrification processes is an increase in the frictional force due to the electrostatic interaction of the contacting surfaces. However, this is not at all the case. The second component of increasing the frictional force is the magnetic attraction of the metal-polymer friction pair as a result of the existence of parallel charges of the same sign on their surfaces. They cause electrical repulsion of friction surfaces. In the case of parallel charges of charges of different sign on the friction surface of the metal-polymer pair, the component of their electrostatic interaction increases and the magnetic interaction decreases.

Ionic adsorption of the liquid phase of constituent components of the friction materials of the patch is characterized by the fact that the solid components present in it adsorb different ions of the same substance in different ways. Thus, ions are capable of polarizing, adsorbed on the surfaces of friction pairs, composed of polar molecules or ions.

Micro-regions of surface friction pairs that carry a certain charge adsorb oppositely charged ions. In this case, the ions of the liquid phase bind the components of frictional materials, which are not charged with the working surface of the lining and are not adsorbed. Under the influence of electromagnetic forces, they remain near the adsorbed ions, forming a double electric layer together with them on the surface of the adsorbent (on the working surface of the rim of the brake pulley). In this case, the adsorbed processes are volumetric [5].

The catalyst for electrons and ions is the inner and outer surfaces of the brake pulley rim. It should be noted that the catalyst does not initiate the interaction of ionized air streams that wash the working surfaces of the brake friction pairs with gas mixtures that have separated from the near-surface layers of the linings. It only accelerates the interaction reactions, which can occur for its absence, but much more slowly.

In the interaction, the friction metal-polymer pairs in the drum and band brake brakes in the range of surface temperatures above the allowable for materials of friction linings are converted into electrochemical systems. In them, reverse cathodic-anode processes occur, and their time charge-discharge characteristics are characterized by an electrochemical cylindrical capacitor. The capacitance in the last double electrical layers is formed in the metal-polymer interface.

The formation of a double electric layer occurs at the interface between two media with different conductivity characteristics of the electronic (metallic friction element) and the ion-electron (surface and near-surface layer of the patch, which are in different thermodynamic states). the surface and near-surface layers of the patches are multicomponent and represent a heterogeneous system in which the consideration of their models must be carried out from the point of view of the chemical kinetics of the oscillation of the reactions. Their chemical potential depends on the concentration of components in the patch.

The average concentration of bonds in contact can be estimated by the ratio of normal load N , Pa to the elastic modulus E , Pa. It is in the range of 10^{-6} - 10^{-3} of the total number of atoms on friction surface 10^{15} per cm^2 . The pulse total repulsive force of these bonds in the direction normal to the contact is equal to the load and the attracting force in the direction of motion of the impulsive friction force. The methods of the theory of nonequilibrium systems make it possible to estimate the dynamic coefficient of friction. For this, let us divide conditionally the bonds into three ensembles with respect to the acting impulse forces. The concentration of repulsive bonds is determined by ratio N , Pa to E , Pa, the pulse total ensemble force is equal to the impulse external load. With electrothermomechanical friction, half of the bonds are at the approach stage, while the surface potential turns spontaneously into the kinetic energy of electrical and thermal vibrations. The probabilities of such oscillations and

the interatomic forces are uniformly distributed in three-dimensional space, that is, the momentum total ensemble force is zero in any direction. The third ensemble is the second half of the bonds that are at the stage of rupture, while work is performed against the impulsive forces of electric attraction and the surface potential is restored. The concentration of bonds in the ensemble is equal to the relative area of N , Pa to E , Pa, the actual contact; the connections are separated and independent. Therefore, when estimating the total breaking strength of an ensemble's bonds equal to the impulsive frictional force, one can use theoretical Frenkel strength σ_m . Then the impulsive friction force is $F_{mp} = \sigma_m N / 2E$, and dynamic friction coefficient $f = \sigma_m / 2E$.

If one assumes Frenkel estimate $\sigma_m = 10^5$ MPa as the theoretical strength of the steel, the bulk modulus of steel $D = 1.7 \times 10^5$, the value of the dynamic coefficient of friction, $f = 0.3$, is obtained. In this case, there is the average value of the dynamic coefficient of friction, which is characteristic of the friction pairs of the band-and-shoe brake of the drilling winch when the drill pipe string is drilled into the well.

4. Conclusion

Thus, the classical approach to the processes of the double electric layer in the "metal-electrolyte-polymer" pair is illustrated, without consideration of the complex heat exchange, to which the metal friction element of the brake devices is exposed.

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