Electrochemistry with double electrical layers in frictional interaction metal-polymer tribolink

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Abstract. The materials of the article illustrate the estimation of the energy loading of a metal friction element in a “metal-electrolyte-polymer” friction pair while forming various types of double electrical layers with the release of its thermal stabilization state. The rapidity of the processes of oxidation and reduction of the working surfaces of friction pairs during their electrothermomechanical frictional interaction leaves an imprint on all other additional processes that subsequently lead to the thermostabilizing and steady state of the metal friction element. Depending on the type of a brake device, the metal friction element has a different metal consumption and the temperature range varies. In addition, it is shown that the materials of the friction pair play an important role in the formation of electric tribosystems, namely: chemical elements that make up the materials, their valence, and the predominant type of intrinsic conductivity, as well as the sign of the electric charge of the friction pair elements that determines the laws of triboelectricity. Thus, an in-depth approach to the evaluation of the thermal stabilization state of a metal element in a “metal-electrolyte” friction pair is shown due to double electric layers that promote the emergence of current densities of different directions.

1. Introduction

In the first part of the article, the authors discussed the following subjects: the nature of the appearance of a double electric layer in the case of electrothermomechanical friction; the structure of a double electric layer on the “metal-electrolyte” boundary with the electrothermomechanical frictional interaction of friction pairs and its mathematical description; a classical approach to the potential jump 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 rapidity of the processes of oxidation and reduction of the working surfaces of friction pairs during their electrothermomechanical frictional interaction leaves an imprint on all other additional processes that subsequently lead to the thermostabilizing and steady state of the metallic friction element.

Depending on the type of the brake device, in which the metal friction element has a different metal content and the temperature range varies. The thermostabilization state of the rear brake drums of KrAZ-250 freight vehicles (AORS-60 chassis) is characterized by temperatures (275.0-325.0) °C during (4.0-6.0) min, which significantly affects the effectiveness of the action, especially in mountainous conditions of operation. With regard to the steady-state temperature of the above-
mentioned brake drum, it does not have a significant effect on the effectiveness of the friction pairs, since it occurs at temperatures (220-390) °C, i.e. lower than permissible for friction linings.

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:
- oxidation-reduction processes in a pair of friction "metal-electrolyte" with frictional interaction;
- structure of the double electrical layer at the boundary of the "metal-electrolyte" phases with the electrothermomechanical frictional interaction of friction pairs;
- approach from the positions of the electrothermomechanical friction approach to the jump in the potential in the friction pair (the "metal-electrolyte" phase) of the friction assemblies and its effect on the state of the metal element;
- effect of the thermal stabilization state of the metal friction element on the internal and external parameters of friction pairs of brake devices.

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

As the materials for the friction pair of the drum-and-shoe brake of the vehicle, the pair "SCH 15-FK-24A" was used.

2.2 Oxidation-reduction processes in a pair of friction "metal-electrolyte" with frictional interaction

The mechanism of the potential jump at the "metal-electrolyte" boundary due to the oxidation and reduction of the metal itself, which is the working surface of the friction element, can be represented as follows. Cations on the working surface of the metallic friction element have an average potential energy reserve corresponding to point 1 in Fig. 1. 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 the repulsive forces, which is expressed by rising energy curve 1-1'. Moving the cation to the right, i.e. detaching it from the working surface of the friction metal element with electrothermomechanical friction with the transition to vacuum, formed as a result of the interaction of the areas of contact spots of the microprotrusions, requires a large work (curve 1-1) of corresponding evaporation energy Uu, energy loading of the working surface of a metal friction element (curve 1'-2).

![Figure 1](image_url)

Figure 1. A scheme of energy change during evaporation of cations of the metal working surface of electrolyte during electrothermomechanical frictional interaction of friction pairs: 1 - the moment of contact of metal with electrolyte 1-2; 1'-2' direct lines of equilibrium in tribo-conjugation

With this energy approach, a temperature gradient changes along the thickness of the metallic friction element from the upper to lower level. The temperature gradient reaches a minimum value at the lower energy level, thus accelerating the steady state of the energy state of the metallic friction
element. In this state, the amount of heat that is generated on the working surface of a metal friction element with electrothermomechanical friction is equal to the amount of heat that is diverted from its outer surface to the environment.

In the first part of the article’s materials, it was stated that during the frictional interaction of "metal-electrolyte" and "electrolyte-metal", oxidative and reduction processes proceed, respectively. 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 U1 and in electrolyte U2. If \( U_1 > U_2 \), then \( \overline{i} > \overline{i} \), i.e., the oxidation process predominates - the transition of metal ions into an electrolyte, the total velocity of which is equal to:

\[
i_1 = \overline{i} - \overline{i} .
\]  

(1)

If \( U_2 > U_1 \), then \( \overline{i} > \overline{i} \), i.e. the reduction process predominates - the discharge of metal ions from the electrolyte, the total velocity of which is:

\[
i_\text{a} = \overline{i} - \overline{i} .
\]  

(2)

As in the first and second case, there are energy levels aimed at reducing them by cooling the working surface of the metallic friction element due to the evaporation of the electrolyte and the transfer of heat to the liquid electrolyte. This is due to the fact that not the entire electrolyte immediately evaporates from the working surface of the polymer lining.

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:

\[
i = \overline{i} = i_0 ,
\]  

(3)

where \( i_0 \) is the exchange current density due to the continuous exchange of ions between the metal and the electrolyte.

2.3 The approach from the positions of electrothermomechanical friction to the potential jump in the friction pair (the "metal-electrolyte" phase) of the friction units of the brake devices

Let us dwell on the physical model of a pair of friction "metal-electrolyte-polymer" of a drum-and-shoe brake of a vehicle. Let us turn to the first part of the material in the article (Fig. 2).

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

With a relative slip of the metal surface, along with the galvano-electromotive force, the thermoelectromotive force will also act (Figure 2), which apparently has an effect on the rate of electrode reactions, interfacial (surface) tension, and so on.
According to Fig. 2, as a rule, quantities $\varphi_{\text{III}}$ and $\varphi_{\text{II}}$ are such that their algebraic sum is not equal to opposite contact potential difference $\varphi_{\text{II}}$. In other words, there is a short-circuited galvanic microelement, which creates the potential for oxidation-reduction reactions to occur on its electrodes. Electromotive force of the element:

$$
\xi_g = \varphi_{\text{III}} - \varphi_{\text{II}} - \varphi_{\text{II}} - \varphi_{\text{II}}.
$$

SN Postnikov in his time stressed that in the scheme in Fig. 3, the electrical capacitances that have interfaces between the spots of the tribocoupling contacts and the electrolyte (double electrical layers) of their leakage resistance, the capacitance between the two electrodes are not shown. All this was taken into account by IM Melnichenko in developing a refined equivalent friction contact scheme with respect to the case of friction under conditions of selective wear, the main component of which is hydrogen wear [1] and mass transfer.

With the same electrochemical behavior of the metal over the entire surface and the presence of contacting islets of EMF galvanoelement:

$$
\xi_g = \xi^0 + \frac{RT}{F} \ln \frac{a_2^{1/n_2}}{a_1^{1/n_1}}.
$$

The averaged value is defined as the difference in electrode potentials, taking into account the inhomogeneity of their processes on adjacent areas of surfaces. The values of this quantity can be judged from the reference literature [2].

The formation of electrical tribosystems is essential for the materials of the friction pair, namely: the chemical elements that make up the materials, their valence, and also the predominant type of intrinsic conductivity (Table 1), as well as the sign of the electric charge of the element - the friction pair, which determines the laws of triboelectricity (Table 2) [3].

| Chemical elements, contained in the alloy | Valence | The predominant type of intrinsic conductivity |
|------------------------------------------|---------|----------------------------------------------|
| C                                        | 2, 4    | Dielectric                                   |
| Al                                       | 3       | n                                            |
| St                                       | 4       | semiconductor n                              |
| Ti                                       | 2, 3, 4 | n                                            |
| V                                        | 5       | p                                            |
| Cr                                       | 3, 6    | n                                            |
| Mn                                       | 2, 3, 4, 6, 7 | n |
| Fe                                       | 2, 3    | n                                            |
| Nt                                       | 2       | n                                            |
| Cu                                       | 1, 2    | p                                            |
| Mo                                       | 6       | p                                            |
| W                                        | 6       | n                                            |

| Table 2. Some regularities of triboelectricity |
|-----------------------------------------------|
| Friction pair                  | Charge sign |
|---------------------------------|-------------|
| Two chemically identical bodies | +           | -           |
| Dielectric - small particles (dust) from the same dielectric | Bigger dielectric | Smaller small particles |
| Dielectric - dielectric        | Dielectric with dielectrical penetration: | Bigger | Smaller |
Dielectric with hardness:

| Metal - Metal | Bigger | Smaller |
|--------------|--------|---------|
| Metal – dielectric | Smaller | Bigger |
| Conductivity type | Dielectric | Metal |
| Metal-semiconductor | n-p or p-n |
| Semiconductor-semiconductor | n-p-n or p-n-p |

In the case of a simultaneous action of galvano-emf $\xi_g$ and thermal emf $\xi_t$, when the appearance of a thermocouple means the transition of a galvanic element to a short-circuit regime, an equivalent circuit corresponds to a three-phase tribosystem in the form of Fig. 4.

Capacitance $C_p$ reflects the ability of the contact spots of the microprotrusions in connection with the increase in their areas of surfaces for accumulating electric charges when a third phase is present in the cavity of the friction capacitor. Electromotive force $\xi_f$ (potential difference $\phi_a - \phi_b$ for $R_0' \rightarrow \infty$) is a kind of the integral parameter that characterizes the conditions under which the process of electrothermomechanical friction proceeds. Its registration with the aid of inertial-free equipment (V amplifier, KK-computer complex) allows one, in particular, to obtain information on the state of thin films on contact areas of microprotrusions.

In addition to the mentioned EMF sources, a unique unipolar generator (conductor L with resistance $R_0'$) plays a special role in friction, which turns into tribo-conjugation if one of its elements and is in a magnetized state (metal friction element). The cause of natural magnetization of bodies can be the magnetic fields of the surrounding ferromagnets, which appeared because of the saturation of parts and assemblies with electrical equipment; fields associated with closed thermoelectric circuits; elastic-magnetic effect, gyromagnetic effect (with very fast rotation); the magnetic field of the earth, and so on.

The distinguishing feature of EMF electromagnetic induction $\xi_f$, in this case in comparison with $\xi_f$, $\xi_n$ and $\xi_g$, firstly, shows that the very fact of its existence does not depend on the presence of direct contact of bodies or the presence of a liquid phase; and, secondly, it is inducted in the mass of one of the friction bodies, which are moving with respect to the magnetized counter-body - the source of the heterogeneous field. Therefore, in the circuit in Fig. 4, source $\xi_f$ can not be connected in parallel to sources $\xi_t$ and $\xi_g$, whereas with source $\xi_g$, for example, one can do this.

![Figure 4. Electric scheme of friction interaction in "metal-electrolyte" friction pairs](image-url)
If in the generalized circuit diagram of the three-phase tribosystem, $R_e'=0$ and $R_0'=0$, it will be single-phase, corresponding to the work of the polymer lining in the range of surface temperatures below the allowable for its friction materials.

A parallel study of mechanochemical and triboelectric phenomena during sliding of a metal friction element along a polymer overlay will allow one to substantiate the nature of the formation of polymer films on the surface of a metal, and vice versa - the transfer of metal to the surface of a polymer lining. Mechanochemical effects boil down to the rupture of carbon-carbon and other chemical bonds in those places of polymer chains where the binding energy is large enough, cracking of chain macromolecules with the appearance of an abnormally high concentration of free radicals and the entry of these radicals into various chemical reactions, including direct reactions with oxidized and juvenile surface of metal in the areas of its outcrop for electrothermomechanical friction and wear, according to the scheme:

$$R-(CH_2)_n-CH_2-Me.$$  

or through the formation of intermediate peroxide radical $R-CH_2-O-O$ - as a result of the addition of oxygen. At the same time, the thermofluctuation acts of the initial decay of overextended polymer molecules, which cause the appearance of the first free radicals in its interlayers, are of great importance. Such acts play the role of a "trigger mechanism" and lead to the rapid decay of many other polymer molecules, which "liberates a large number of elastic mechanical energy concentrated in them." Isolation of the latter (in the form of heat) promotes the polymerization of fragments of macromolecules, which can go along the path of formation of secondary structures that differ markedly in their physical properties [5].

The steady-state friction regime in the "metal-polymer" system corresponds, apparently, to some dynamic equilibrium of the rate of decomposition and formation of polymers (copolymers), to which the degree of electrification and its sign have the most direct effect. Indeed, the sliding of the metal along the overlay is accompanied by a significant violation of the electron density at each point of frictional contact of the microprotrusions. The transfer of charges through the interface can occur both in that and in other direction; depending on this, the polymer is charged either positively or negatively with respect to the metal body co-tied to it. Therefore, these are polymers conventionally divided into electropositive and electronegative; pumping, for example, electrons to the interface from the side of the organic compound is quite possible due to the movement of electrons along the chain of the macromolecule of the covalent bond line and the transitions between neighboring long-chain molecules. As for the free electrons charging by the surface layer of the metal, it depends on the electrical capacity of the metallic friction element and can occur indefinitely if the latter is connected to such practically "bottomless" reservoir of electric charges as, say, Earth. The acquisition of a potential of several thousand volts by the dielectric surface indicates the existence of a "working surface of a metal friction element - the working surface of a polymer lining" between the friction capacitor plates and between their microprotrusions of a very strong electric field that activates erosive and diffusion processes and, most importantly, the transfer of metal electrons to the electronegative polymer or, conversely, the electropositive products of the thermome anodestruktii polymer to the metal surface with formation of the vaniem-protective film thereon. The strength of this film depends on the reactivity of carbon atoms with unsaturated valence bonds and, to some extent, if one takes into account the reversible reduction of homogeneous chains and the appearance of new heterogeneous molecules - from the adhesive activity of functional groups of polymeric materials. In this case, the surface of the polymer patch never returns to its original structural state.

3. Results and discussion

The kinetics of mechanochemical and triboelectric phenomena is reflected in the behavior of the dynamic friction coefficient, which determines the order of the forces opposing slip and applied to the metal-polymer three-boisystem. Some of the above-mentioned representations were a small series of discoveries, the main points of which are the following:

- with the thermal resistance of the contact of metal-polymer friction pairs and the accumulation of heat in the temperature zone higher than that permissible for materials of surface and near-surface
layers in the friction zone, there are many microthermal batteries with different energy activity that promote inversion of heat fluxes from polymer to metal and the appearance of stable thermal stabilization at the minimum temperature gradient on the thickness of the metallic friction element [6];

- the electrothermal resistance of discrete contacts, arising from friction with different energetic activity of micro capacitors and thermobaths with instantaneous switching, when the areas of five contacts of microprotrusions and the gradient of mechanical properties change, as well as the rate of penetration of interacting pulses of electric and thermal currents, determine the wear rate microprotrusions during repolarization, leading to destabilization of the dynamic coefficient of friction of metal-polymer friction pairs.

- at various energy levels of surface and near-surface layers of metal-polymer friction pairs, the stages of the process of electrothermomechanical friction are generated, developed and performed in a certain sequence of effects with special transient processes, superposition principles and the appearance of side effects, while changing the current lines of dynamic, electric, magnetic, thermal and chemical fields interacting with the lines of currents of the velocity field of the washing media obeys the wave nature of phase shift;

- the products formed under the influence of frictional electrothermic explosion, falling into the gaps between microprotrusions of friction pairs, contribute to the generation of a volumetric electrical charge and the appearance of an electrothermal discharge, which leads to the breakdown of the layer of the remaining products and their mass transfer to the working surface of the friction element of the friction pair.

4. Conclusion
Thus, an in-depth approach to the evaluation of the thermal stabilization state of a metal element in a metal-electrolyte friction pair is illustrated by double electrical layers that contribute to the appearance of current densities of different directions.

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References
[1] Kindrachuk M V, Volchenko D A, Volchenko N A, Stebeletskaia N M and Voznyi A V 2017 The influence of hydrogen on the wear resistance of materials in friction pairs of braking devices Physico-chemical mechanics of materials 135 - 141
[2] Luschekin G 1988 Methods for studying the electrical properties of polymers (Moscow: Chemistry)
[3] Kudin V I, Martinovich V A 2008 Electrical properties of metals and semiconductors (Minsk: BNTU Publishing House)
[4] Dzhanakhmedov A H, Volchenko A I, Vozny AV, et al. 2016 Design and verification calculation of friction units for drum and disk brake equipment of vehicles. Standard (Baku: Apostroff)
[5] Mashkov Yu K 2013 Tribophysics of metals and polymers (Omsk: Izd-vo OmGPU)
[6] Volchenko A I, Kindrachuk M V, Volchenko D A, Volchenko N A 2012 Diploma No. 444 for the scientific discovery "The phenomenon of thermal stabilization in metal-polymer friction pairs" Examination of the application for discovery No. A-588 dated 05.09.2012. (Moscow: International academy of authors and scientific discovery and the invention) -