

Non-Equilibrium Thermodynamics with Linear Modes in Tribo-couplings (Part I)

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Abstract

The article examines the following questions: thermal conductivity and thermoelectric phenomena in tribo-couplings; electro-kinetic phenomena and chemical reactions in tribo-couplings; the discussion of the results. An algorithm of non-equilibrium thermodynamics is proposed, which contains thermal conductivity and thermoelectric phenomena in a non-massive metal friction element and electrokinetic phenomena in the near-surface layers of a polymer lining. In linear modes of operation of friction pairs of brakes, it is shown that due to the cross effect with temperature gradients for metal elements, two equilibrium states are revealed - a steady surface temperature and a thermal stabilization state; for a polymer lining, the equilibrium state is considered to be the burnout of the binder components from its near-surface layer with the formation of liquid islands. The flow of electrokinetic phenomena in the near-surface layer of the polymer lining and the determination of: the potential of the fluid flow and the resulting electric current; effect of electro-osmosis and liquid pressure. From the above parameters, ratios are formed that are equal to the Onsager and Saxen ratios, which makes it possible to determine the parameters by calculation.

Keywords: nonequilibrium thermodynamics, linear mode, friction pair, metal and polymer friction elements.

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Triboqovşaqlarda xətti rejimli qeyri-müvazinat termodinamikası (I hissə)

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Xülasə

Məqalədə, triboqovuşmalarda istilik keçiriciliyi və termoelektrik hadisələr; elektrokinetik hadisələr və kimyəvi reaksiyalar nəzərdən keçirilib. Qeyri-müvazinat termodinamika algoritmi təklif olunub ki, bu alqoritmə qeyri-kütləvi metal friksion elementində istilik keçiriciliyi və termoelektrik hadisələr, polimer kündenin üst təbəqələrində elektrokinetik hadisələr mövcuddur. Onsager və Saksen nisbətlərinə bərabər olan nisbətlər formalaşdırılmışdır ki, bu da parametrləri hesablama yolu ilə müəyyənləşdirməyə imkan verir.

Açar sözlər: qeyri-müvazinat termodinamika, xətti rejim, sürtünmə cütü, metal və polimer friksion elementlər.

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Неравновесная термодинамика с линейными режимами в трибосопряжениях (часть I)

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Аннотация

В статье рассматривается: теплопроводность и термоэлектрические явления в трибосопряжениях; электрокинетические явления и химические реакции в трибосопряжениях. Предложен алгоритм неравновесной термодинамики, который содержит теплопроводность и термоэлектрические явления в немассивном металлическом фрикционном элементе и электрокинетические явления в приповерхностных слоях полимерной наклейки. Сформированы отношения, которые равны соотношениям Онсагера и Саксена, что позволяет определять параметры расчетным путем.

Ключевые слова: неравновесная термодинамика, линейный режим, пара трения, металлический и полимерный фрикционные элементы.

Introduction

For the state of friction pairs of brakes close to equilibrium, a general theory can be formulated based on linear relations (Onsager and Saxen) as applied to a metal friction element and a friction lining. In this case, non-massive metal friction elements are considered. For the latter, an equilibrium state is observed for a steady surface temperature, when its gradient becomes minimal.

The second equilibrium state is thermally stabilized, when the minimum temperature gradient is reached across the thickness of the metal friction element. As for the friction lining, its near-surface layer undergoes destructive changes at a temperature above the permissible one [1].

Analysis of literature data and statement of the problem

The study [2-6] indicates that with an increase in the relative humidity of the air in friction pairs, an increase in the wear of their working surfaces is observed, caused by an increase in the friction moment. In addition, it is noted that an increase in environmental humidity can cause an increase in the wear of a polymer friction element by more than 200 times [1].

At the same time, it was noted in [2, 5] that with an increase in the partial pressure of water vapor in the intercontact gap of friction pairs, the friction moment decreases, and, consequently, the wear of the friction material decreases.

Thus, it follows from the considered works that the relative humidity of the air entering the intercontact zone of friction pairs carries an additional load and causes a change in their operating parameters.

The effect of moisture on the tribological parameters of friction units of brake devices must be considered through the prism:

- corrosion due to exposure to moisture, salt or other environmental components;
- direct conversion of thermal energy into electrical energy in friction pairs;
- electric balance of currents in the zone of contact of friction pairs;
- intercontact gaseous medium in friction units;
- nanotribological processes that occur on the working surfaces of friction pairs and in the near-surface layers of friction linings.

All this must be considered from the point of view of the influence of nonequilibrium thermodynamics on the energy load of friction pairs of brakes with linear operating modes in their tribocouples. The paper [7] illustrates the equilibrium and nonequilibrium statistical mechanics as applied to the surface layer of a polymer lining, which is in the solid state and in phase transitions of the 1st and 2nd order.

Using the mathematical apparatus, taking into account the electrons and ions of the surface layer of the overlay, a consistent system of three states is built, the criterion for evaluating which is the thermodynamic limit.

However, none of the listed works noted cross effects in tribocouplings and the determination of relative parameters relating to the thermal conductivity of metal friction elements and thermokinetic phenomena in the near-surface layer of the polymer lining.

This is achieved using the Onsager and Saxen relations, when triboconjugations are considered from the standpoint of nonequilibrium thermodynamics with linear loading modes [8].

Formulation of the problem

Main questions of the article: thermal conductivity and thermoelectric phenomena in tribocouplings; electrokinetic phenomena and chemical reactions in tribocouplings; the discussion of the results.

Objective – substantiation of the possibility of using non-equilibrium thermodynamics with linear regimes in tribocouplings of friction pairs of brakes.

Modes of operation of friction pairs of brake devices

The modes of operation of the drum-and-disk-shoe brakes of vehicles, as well as the band-shoe brakes of drawworks are aperiodic cyclic. The testing of braking devices of vehicles is carried out according to the standards of the United Nations Economic Commission for Europe [6] on three types of modes: "0", "I", "II". The zero type of test refers to the preliminary. Both during the first and second types of testing of drum and disc brakes of vehicles, temperatures develop on their friction surfaces that exceed those allowed for friction lining materials. However, they do not reduce the effectiveness of drum and disc brakes due to the ingress of moisture on their working surfaces during the movement of vehicles.

Stabilization thermal state of the metal friction element corresponds to thermodynamic equilibrium, in which the internal parameters of the system are the same. In this case, the brake drum or brake pulley have a complex shape and all their internal parameters do not depend on the coordinates. From this point of view, the process of establishing thermodynamic equilibrium can be considered as a process of equalizing

internal parameters, which is accompanied by the transfer of thermal energy from metal friction elements to their flanges and fastening protrusions until we have a negative heating rate of the metal friction element with a positive heating rate of its flange. It is known that in thermodynamic processes temperature is defined as a parameter whose constancy characterizes the position of thermodynamic equilibrium. In addition, the temperature equalization of metal friction elements and their flanges and mounting protrusions is accompanied by convective and radiative heat transfer from their matte surfaces. From this point of view, temperature belongs to generalized thermodynamic potentials, and its deviation from the equilibrium level determines the intensity of the heat transfer process [6-8] depending on whether the metal friction element is heated or forced to cool.

Initially, consider the process of heating a metal friction element. In the steady state, the energy W_p entering the system from the outside, due to the dissipation of mechanical energy into thermal energy during the implementation of specific loads ($W_H + \Delta W$) in the friction units of the brake devices, should dissipate into the environment from the matte surfaces of the metal friction elements.

When a disturbance appears in the tribosystem (in the form of water drops or thermal-oxidative destruction of the binder components of polymer friction materials at temperatures above the permissible level), the thermal state of metal friction elements changes. Let us assume that the perturbation manifests itself in a change in only one parameter Π , i.e., the surface temperatures of the metal friction elements, and it is they that determine their further thermal regime. It was further established that the change is small,

i.e., that only such deviations are considered at which the segments of the temperature curves that determine the thermal regime can be considered linear. In a disturbed thermal regime, when energy is redistributed between the matte and polished surfaces of a metal friction element due to the forced cooling of the latter (when ΔT appears), this balance is disturbed, since the properties of the tribosystem change, in which energy is absorbed. If the properties of the tribosystem are such that the energy consumption $W=W_H + \Delta W$ after the deviation of the thermal regime (after the disturbance) will occur more intensively than the increase in energy $\Delta W_H=f(T)$, which the next interaction of friction nodes can give after the disturbance, then the new (perturbed) the thermal regime leads in the tribosystem to maintaining the previous thermal regime (or a regime close to it), i.e. tribosystem will be stable. From this definition of stability (stability) it follows that the mathematically written condition for its conservation, or. as they say, the criterion of stability K will be the condition

$$\Delta W / \Delta T > \Delta W_H = \Delta T$$

or in differential form $d(V_p - W)dT < 0$.

We introduce the notation $W_p - W = \Delta W_E$ and call it excess energy. This energy is positive if the additional energy of the thermochemical reaction of destruction of the binding components of the materials of the friction linings and radiation heat exchange between the working surfaces of the friction pairs of the brake device will increase more intensively than the load energy of the tribosystem, including losses for friction work in its friction units. The stability criterion is now written in the form

$$K = \frac{d(\Delta W_E)}{dT} < 0 \quad \text{or} \quad K < 0.$$

The thermal regime is stable if the derivative of the excess energy with respect to the defining parameter T , i.e., the temperature is negative for the polished surfaces of the friction metal element of various types of brake devices. It should be noted that a small fraction of the energy of the metal friction element is spent on the formation of a double electric layer according to the scheme "the polished surface of the metal friction element is the working surface of the friction lining" [9].

A sharp change in the specific fractions of the heat of the working area of the friction lining, which goes to the accumulation of heat with the surface layer, can be traced in the middle of the long test mode of the drum-shoe brake, after which the heating rate stabilizes and becomes equal to the lower level of the surface layer of the lining. This is explained by the fact that in the surface layer of the lining begins the interaction of the components of friction materials, which are in the nature of endothermic reactions.

At the same time, a significant part of the energy goes to the formation of a double electric layer "the working surface of the friction linings (not interacting with the metal friction element) - the lower level of the surface layer of the linings", as well as to the release of the gas mixture and its ionization, and to the desorption of moisture from liquid fractions formed in the surface layers of the overlays.

In addition, in the future, after half the time of prolonged heating, the inversion of electrization currents is possible according to the scheme "polished surface of a metal friction element - ionized gaseous medium", and moisture desorption - "working surface of friction linings - lower level of the near-

surface layer of linings” with a positive quasi-stable their heating rate.

As for the cooling rates of the working zone of the near-surface layer and its lower level of the friction lining, by the end of the fourth minute (after completion of the tests) they stabilize at negative cooling rates.

Energy ΔW_E should be determined for the tribosystem as a whole, taking into account all the influencing processes (heating, cooling, radiative heat transfer and thermochemical destruction of the binding components of the friction material) - working surfaces of linings" ($K < 0$) (and interacting with a metal friction element) and "working surfaces of linings - a metal friction element", interconnected by an ionized gas mixture and moisture desorption. The inversion of the currents is carried out in the opposite direction, i.e., the sign of the electrification currents changes.

Carried out according to the above criterion of stability (stability) of the tribosystem according to the ratio: the emissivity coefficients of the polished and matte surfaces of the metal friction element and the energy of thermochemical reactions occurring during the destruction of the binder components located in the friction lining and

their energy characteristics in pure form, i.e. without structural connections with other components in the lining, shows the intensity of the external impact on the tribosystem from the point of view of stabilizing the thermal state of its metal friction element when the physical and chemical properties of the surface layers of the friction linings change.

Thermal conductivity and thermoelectric phenomena in tribocouplings

Let us dwell briefly on the basic principles that take place in thermal problems.

Reciprocity is used in solving some problems of heat conduction; this means that if the heat source I_s located at point 1 causes a temperature change $\Delta t = f(\tau)$ at point 2, then if the source is moved to point 2, the same temperature change Δt will occur at point 1.

It should be emphasized that at mutual points the rates of temperature change are the same, but the temperature gradients are different, so it must be remembered that the transition to a mutual problem is not a transition to an equivalent problem - the temperature fields turn out to be different.

The importance of applying the reciprocity principle in problems of heat conduction is known [1].

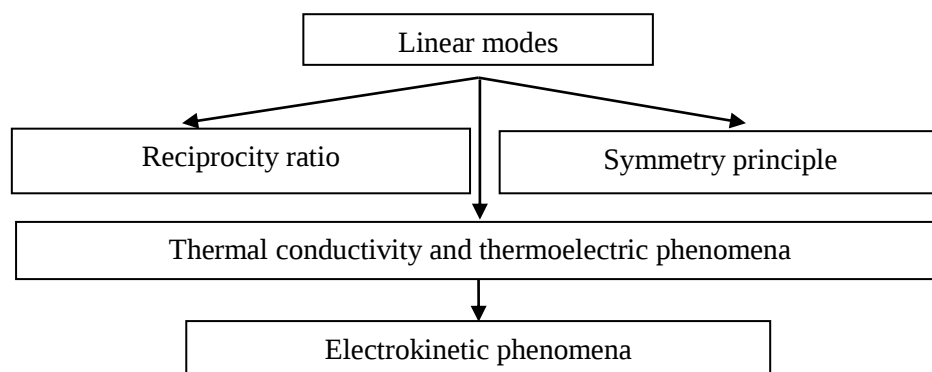


Figure 1 – Algorithm of nonequilibrium thermodynamics with linear regimes in tribocouplings

These include under the action of a heat source: in a semi-limited body or in an unlimited plate; a plate covered with a layer of turbulent fluid, as well as in a plate in the presence of a fluid layer and an adiabatic condition on one boundary, and a type III-rd boundary condition on the other.

Symmetry - proportionality, proportionality of the parts of the product located on both sides of the middle of the center. On fig. 1 shows the algorithm of non-equilibrium thermodynamics in triboconjugations of brake friction pairs.

In metal friction elements of brake devices, the heat flux may differ in direction from the temperature gradient; a temperature gradient in one direction can cause heat flow in the other direction. Entropy production is determined by the expression

$$\sigma = \sum_{i=1}^k J_{qi} \frac{\partial}{\partial x_i} \left(\frac{1}{T} \right), \quad (1)$$

where J_{qi} – heat flow; x_i – Cartesian coordinates; T – surface temperature.

The heat flux for a discrete system of tribocoupling is determined from the expression

$$J_{qi} = \sum_k L_{ik} \frac{\partial}{\partial x_k} \left(\frac{1}{T} \right) = \sum_k \left(\frac{-L_{ik}}{T^2} \right) \frac{\partial T}{\partial x_k}, \quad (2)$$

where L_{ik} – Onsager ratio.

For anisotropic solids, the thermal conductivity is a second rank tensor. Fourier's law in this case is written as

$$J_{qi} = - \sum_k k_{ik} \frac{\partial T}{\partial x_k}, \quad (3)$$

Based on comparison (2) with (3), we obtain the equality

$$L_{ik} = T^2 k_{ik}. \quad (4)$$

The reciprocity relation $L_{ik} = L_{ki}$, then means that

$$k_{ik} = k_{ki}, \quad (5)$$

i.e., thermal conductivity is a symmetrical tensor. For many metallic friction elements, their symmetry of their crystal structure implies that $k_{ik} = k_{ki}$. However, this does not at all mean confirmation of the reciprocity relations, since it follows from the trigonal, tetragonal, and hexagonal symmetry of crystals that

$$k_{12} = -k_{21}. \quad (6)$$

If the reciprocity relations are valid, then

$$k_{12} = k_{21} = 0. \quad (7)$$

Equation (7) implies that a temperature gradient in the x direction causes a heat flow in the positive y direction, but a gradient in the y direction causes a heat flow in the negative x direction. It follows from Onsager's reciprocity relation that the validity of the reciprocity relation is confirmed.

A parameter such as the temperature gradient ($1/T$) in the interface of friction pairs can cause a heat flow, but also other flows, such as an electron flow, and as a result, an electric current. The thermoelectric effect is one of the cross effects, in which the temperature gradient causes not only a heat flux, but also an electric current, and vice versa (Fig. 2 a, b).

Thermoelectric effect is a cross effect between thermodynamic parameters, heat and electric flows. According to fig. 2 a shows the Seebeck effect, in which two dissimilar metal conductors are connected in a circuit, and each connection is at different temperatures.

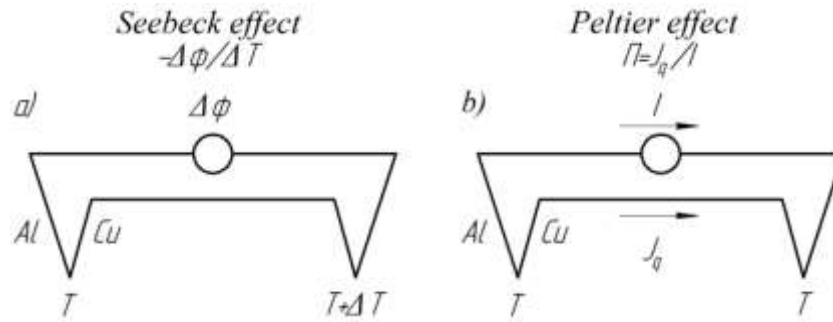


Figure 2 a, b – Basic thermoelectric phenomena in tribo-couplings

As a result, an EMF is generated. The last component, $\sim 10^{-5}$ V/K, may differ from sample to sample. In the Peltier effect (Fig. 2 b), two compounds are at the same temperature and a current passes through them.

Electric current leads to the appearance of a heat flow from one connection to another. The Peltier heat flux is typically $\sim 10^{-5}$ J/(s·A).

The Seebeck effect gave rise to the Peltier effects and the accompanying Thomson, Joule - Lenz effects. The last two are that if there is a temperature difference along the conductor through which the electric current flows, then heat is released or absorbed (depending on the direction of the current) in the volume of the conductor.

To reduce the effect of heat on electrical circuits, the distribution of the Peltier effect is used, which consists in the uneven presence of the concentration of alloying elements in the branches of the electrical circuit.

According to Table 1 Osnager reciprocity relations for Cu-Al thermocouple is the minimum value (0.77), and for the Cu - Bi thermocouple - the maximum value (1.0 V) due to the different position in the table of D.I. Mendeleev and a significant difference in atomic weights.

Table 1 – Experimental data confirming the Osnager reciprocity relations when operating thermocouples in a linear mode

Thermocouple	$T, ^\circ\text{C}$	$\Pi/T, \mu\text{V/K}$	$-\Delta\phi/\Delta T, \mu\text{V/K}$	L_{qe}/L_{eq}
Cu – Al	15,8	2,4	3,1	0,77
Cu – Ni	0	18,6	20,0	0,930
Cu – Ni	14	20,2	20,7	0,976
Cu – Fe	0	-10,16	-10,15	1,00
Cu – Bi	20	-71	-66	1,08
Fe – Ni	16	33,1	31,2	1,06
Fe - Hg	18,4	16,72	16,66	1,004

The design of the drawworks band-shoe brake has symmetry (Fig. 3). The symmetry of the design does not mean that the energy load of the left and right brakes is the same due to the non-equilibrium thermodynamics that take place in their friction pairs.

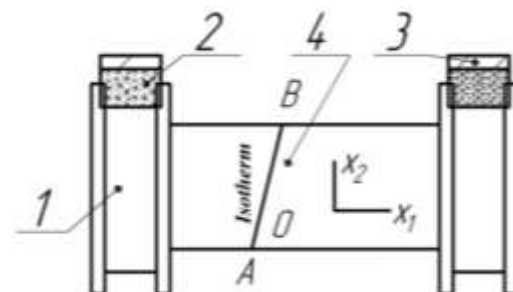


Figure 3 – Symmetrical arrangement of band-shoe brakes in a drawworks: 1 – brake pulleys; 2 - friction lining; 3 - brake band; 4 – drum

Electrical phenomena in tribocouplings

Electro-kinetic phenomena correspond to the interaction between the microelectric current and the flow of liquid entering the interfaces of friction pairs.

Let us consider two parts of the friction lining 1, 2 (Fig. 4 a), separated by a porous partition. If a voltage V is applied between the two parts of the lining 1 and 2, then the current flows until the pressure difference Δp takes a stationary value. This pressure difference is called electroosmotic pressure.

On the contrary, if the fluid flow J from one part of the lining 1 to another 2 is created by the specific loads of the metal friction element 3 (Fig. 4 b), then a microelectric current flows between the electrodes, called the flow current. The electroosmotic effect is successfully used to remove moisture from the friction surfaces of interfaces of braking devices [10].

As before, the thermodynamic description of these effects begins with a formula for the production of entropy under the above conditions. In this case, we have an essentially discrete system in which there are no gradients, but there is a difference in chemical potentials between the two parts of the patch.

For discrete systems, which are friction pairs, the entropy production per unit volume s is replaced by the total entropy production $d_i S/dt$.

In addition, the entropy produced by the flow from the first part of the lining to the second can be formally represented as a chemical reaction, for which the difference in electrochemical potentials is converted into affinity.

In this way,

$$\frac{d_i S}{dt} = \sum_k \frac{\tilde{A}_k}{T} \frac{d\xi_k}{dt}, \quad (8)$$

where

$$\tilde{A}_k = (\mu_k^1 + z_k F \phi_1) - (\mu_k^2 + z_k F \phi_2); \quad (9)$$

$$d\xi_k = -dn_k^1 = dn_k^2. \quad (10)$$

In the given dependences, the superscripts indicate two volumes of the overlay: z_k is the ion charge of component k , F is the Faraday constant, and ϕ is the electric potential.

For a relatively small pressure difference between the two parts of the patch, since $(\partial\mu_k/\partial p) = v_k$ is the partial molar volume, we can write

$$(\mu_k^1 - \mu_k^2) = v_k \Delta p \quad (11)$$

Dependence (9) after transformations has the form

$$\frac{d_i S}{dt} = \frac{1}{T} \sum_k \left(-v_k \frac{dn_k^1}{dt} \right) \Delta p + \frac{1}{T} \sum_k (-I_k) \Delta \phi \quad (12)$$

where $\Delta \phi = \phi_1 - \phi_2$ и $I_k = z_k F n_k^1 / dt$ - electric current due to fluid flow k .

After a series of substitutions and transformations, calculated dependencies (13-18) were obtained (Table 2).

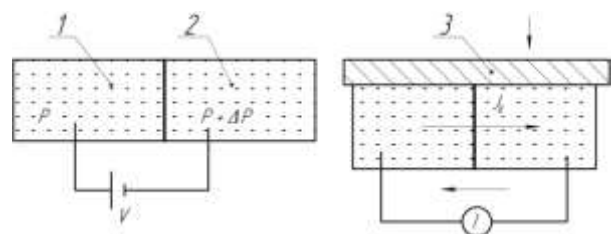


Figure 4 a, b – Electrokinetic phenomena in a friction lining at rest (a) and under the action of specific loads (b) in a friction pair: 1 - friction lining; 2 - capillary; 3 - metal friction element

Table 2 – Parameters and their ratios in friction linings of tribocoupling

Parameters and ratios		Estimated dependencies	
Onsager relations	Flow potential	$\left(\frac{\Delta\phi}{\Delta p}\right)_{I=0} = -\frac{L_{12}}{L_{11}} = 0,95 ;$	(13)
	Electroosmosis	$\left(\frac{J}{I}\right)_{\Delta p=0} = \frac{L_{12}}{L_{11}} = 0,97 ;$	(14)
	Electroosmotic pressure	$\left(\frac{\Delta p}{\Delta\phi}\right)_{J=0} = -\frac{L_{12}}{L_{22}} = 1,06 ;$	(15)
	Fluid flow current	$\left(\frac{I}{J}\right)_{\Delta\phi=0} = \frac{L_{12}}{L_{22}} = 1,04 ;$	(16)
Saxen ratios		$\left(\frac{\Delta\phi}{\Delta p}\right)_{I=0} = -\left(\frac{J}{I}\right)_{\Delta p=0} = 0,9 ;$	(17)
		$\left(\frac{\Delta p}{\Delta\phi}\right)_{J=0} = -\left(\frac{I}{J}\right)_{\Delta\phi=0} = 0,98 .$	(18)

The friction lining FK-24A, located on the incoming branch of the brake band, was studied at a surface temperature of 390 - 430° C, when formaldehyde resin burned out from the surface of the lining and the formation of liquid islands was observed (see Table 2) at a difference in specific loads of 0,3 MPa between the incoming and outgoing surface of the lining showed the following:

- the Onsager ratio for the considered parameters varied from 0,95 to 1,06;
- dependencies (17, 18) are called the Saxen relation and when using the formalism of nonequilibrium thermodynamics, their validity is more general and their values vary from 0,9 to 0,92.

Discussion of results

Studies of non-equilibrium thermodynamics with linear regimes in tribocouples of friction pairs based on the reciprocity relation and symmetry principles made it possible to establish the following:

- an algorithm of non-equilibrium thermodynamics is proposed, which contains thermal conductivity and thermoelectric phenomena in a non-massive metal friction element and electrokinetic phenomena in the near-surface layers of a polymer lining;
- in linear modes of operation of friction pairs of brakes, it is shown that due to the cross effect with temperature gradients for metal friction elements, two equilibrium states are revealed - a steady surface temperature and

a thermal stabilization state; for a polymer lining, the equilibrium state is considered to be the burnout of the binder components from its surface layer with the formation of liquid islands;

- the flow of electrokinetic phenomena in the near-surface layer of the polymer lining and the determination of: the potential of the liquid flow and the resulting electric current; effect of electroosmosis and liquid pressure;

- from the above parameters, ratios are formed that are equal to the Onsager and Saxen ratios, which makes it possible to determine the parameters by calculation.

Conclusion

Systematize and present in the form of algorithms, perturbations, potentials and gradients in the energy fields of metal-polymer friction pairs. The maximum energy load of metal friction elements and their heat transfer capacity, consisting in the combined action of conductive heat transfer with radiative and convective heat transfer from their surfaces, as well as the allowable temperature for polymer lining materials.

The initial conditions for a metal friction element must be variable, which would correspond to its steady state and its thermal stabilization state.

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