Molecular Mechanisms of Self-Organization in Friction. Part VII. Fluctuations of the Tribo-EMF and Stepwise Coagulation of Copper Nanoclusters when the Servovit Film Appears under the Effect of Wearlessness

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Abstract—The mechanism of the appearance of tribo-EMF autooscillations in steel–copper-alloy pairs in the case of self-organization in the wearless and transient friction modes is proposed; the mechanism is based on the assumption of the periodic coagulation of copper nanoclusters on the friction surface when the servovit film forms. It is shown that the governing parameter of the self-organization and the cause of tribo-EMF autooscillations in the studied tribosystems is periodic variation of the electrolyte concentration in the diffusion layer of the metal-cladding lubricating material.

Key words: self-organization, friction, selective transfer, nanostructure, copper cluster, tribo-EMF, tribochemical reaction.

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INTRODUCTION

The specific role of electrochemical processes and their mechanisms in generating boundary layers on metallic friction surfaces, in the general case and in the wearless friction mode specifically, is discussed in a variety of publications (references in [1-3]). In work [4], Rosenberg notes that researchers in the field of friction and wear should bear in mind the "... electric and electrochemical phenomena and processes of adsorption and other types of sorption on the rubbing surface that inhibit, or, on the contrary, intensify wear "The same work references the work of Rebinder and Venstrem, where the interrelation between the tribological and electrochemical properties of tribocouples is illustrated experimentally [4]. Later Dubinin examined thoroughly the causes of the electric field in tribosystems; the results of study of the effect of electric phenomena on the friction process were published in [5, 6]. At present it is evident [1-3] that electrochemical mechanisms govern the process of self-organization of copper-alloy-glycerin-steel tribosystems. In such systems, self-organization manifests itself particularly in the oscillatory pattern of changes of the electrode potential of the friction surface in the process of the appearance of the servovit film during selective transfer (the effect of wearlessness in friction).

The mechanism of self-organization governing the gradient of the electrolyte solution concentration in the lubricating material layer in the gap between contacting metals is proposed in [7] to explain the synchronous auto-oscillations of the friction coefficient and electric resistance in the bronze–steel friction pair lubricated with nanosized copper clusters dispersed in an aqueous glycerin mixture.

The present paper uses this approach to explain the tribo-EMF auto-oscillations occurring during selforganization under wearless friction conditions in the transient mode in the bronze–steel pair lubricated by dispersed nanosized copper clusters in an aqueous glycerin mixture.

EXPERIMENTAL

Investigation of the triboelectric properties of the bronze–alcohol–steel system in the selective transfer mode leading to wearless friction was conducted on a TR-2 tribometer [8]. The time dependences of the friction coefficient and tribo-EMF of the bronze–steel pair were registered at constant temperature; the load was increased and reduced regularly within the range from 0 to 25 MPa at the rate 0.03–0.06 MPa/s. The sliding velocity was set within 0.6–4.0 m/s. Polyatomic alco-



Fig. 1. Kinetic dependences of tribo-EMF (1), friction coefficient (3), and force of friction (4) in the bronze–glycerin–steel tribosystem and their correlation with load variations (2) at V = 0.6 m/s; T = 333 K.



Fig. 2. Kinetic dependences of tribo-EMF (1), friction coefficient (3) and force of friction (4) in the bronze–butandiol-1,4–steel tribosystem and their correlation with load variations (2) at V = 0.6 m/s; T = 293 K.

hols (propanediol-1,3, butanediol-1,4, and glycerin) served as a lubricating fluid. Figures 1 and 2 show the kinetic dependences of the tribo-EMF and the coefficient and force of friction.

The structure and morphology of the copper nanoclusters were studied with the method of atomic force microscopy (AFM) on a Solver P47 Pro scanning probe microscope in the half-contact mode (probes of the type NSG 10/NSG 11). The topography and phase contrast of the copper coated by vacuum sputtering (UVN 71P unit, coating thickness $\approx 2 \ \mu$ m) on glassceramic substrates (purity class 14) with dimensions 10 × 10 mm were visualized simultaneously. The AFM scans (except for scanning artifacts) were processed and quantitative amplitude relief characteristics were obtained using the Image Analyses software package supplied by ZAO Nanotechnology MDT.

Stable suspensions of the copper nanoclusters in the glycerin aqueous solution were obtained with the

known method [9] of electrolysis of the glycerin aqueous solution on copper electrodes in an ultrasound field (the UZDN-1 apparatus).

RESULTS AND DISCUSSION

In addition to its usefulness as a diagnostic parameter for monitoring friction conditions [8], tribo-EMF is itself an important parameter in the study of the evolution of tribosystems, particularly their self-organization. This is because the friction process exerts a continuous effect on the surface condition of the electrodes, while the servovit film appearing during self-organization in the wearless mode ensures parallel actuation of a large and continuously varying number of micro-EMF sources, which appear between the copper coating spots, and the absence of such sources on the friction surface. Registration of the EMF makes it possible to make judgments about the contact surface in situ.

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The presented results show (Figs. 1, 2) that the functioning of self-organizing tribosystems is accompanied by tribo-EMF changes due to load or pressure variations in the contact zone, or, which is the same, with variations in the quantity and physicochemical nature of triboelectricity sources on the contact surface. The general tendency of the integral tribo-EMF to grow as the pressure increases is accompanied by strongly pronounced chaotic auto-ocsillations.

In accordance with the Nernst equation [10], ΔE_{spon} , the superconductivity of the EMF of the galvanic element resulting from the spontaneous process is expressed as

$$\Delta E_{\rm spon} = \Delta E_0 - \frac{RT}{nF} \ln \frac{[{\rm Me}_{\rm akt}^{n+}]}{[{\rm Me}^{n+}]},$$

where ΔE_0 is the standard EMF of this element; [Me^{*n*+}_{akt}] is the concentration of cations of the more active metal in the anode space; [Me^{*n*+}] is the concentration of cations of the less active metal in the cathode space; *n* is the valence of the cations; *T* is temperature; *R* is the universal gas constant; and *F* is the Faraday number.

During friction of copper alloys (bronze and brass) on steel, the more active metals are Fe, Sn, Zn, and the less active is Cu. Note that both can be differently oriented by the molecules of the lubricating material and products of its decomposition. Therefore, their electrode potentials vary as the chemical composition of the lubricating medium changes both during transition from one lubricating material to another and in the process of friction due to the tribochemical reactions evolving in the contact zone.

The following can be recorded for the ΔE sum of the spontaneous ΔE_{spon} and nonspontaneous $\Delta E_{\text{non-spon}}$, i.e., the friction-initiated EMF:

$$\Delta E = \Delta E_{\rm spon} + \Delta E_{\rm non-spon},$$

on the one hand, and, on the other hand,

$$\Delta E = \Delta E_0 - \frac{RT}{nF} \ln a \frac{[\mathrm{Me}_{\mathrm{akt}}^{n+}]}{[\mathrm{Me}^{n+}]}.$$

Then,

$$\Delta E = \Delta E_0 - \frac{RT}{nF} \ln \frac{[\mathrm{Me}_{\mathrm{akt}}^{2+}]}{[\mathrm{Me}^{n+}]} - \frac{RT}{nF} \ln a,$$

where the value *a* indicates how many times the ratio between the concentrations of the active and less active metals changes under the effect of friction compared with its absence at the given moment of time. Here and later, $\Delta E_{\text{non-spon}} = -\frac{RT}{nF} \ln a$ is the contribution of the friction-initiated nonspontaneous process into the tribo-EMF.

The results of experiment [11] and the data in Figs. 1, 2 show that the tribo-EMF is $(0.5-1.5) \times 10^{-3}$ when the load grows from 0 to 10–20 MPa.

Applying the Nernst equation to the process in question and substituting the constants, it can be recorded that, at room temperature,

$$\Delta E = \Delta E_{\rm spon} - \frac{0.059}{2} \log a.$$

Taking into account that the nonspontaneous tribo-EMF change is determined primarily by the change in the ratio between the concentrations of the potentials of the determining ions, we obtain that, in order that ΔE grow within the range $(0.5-1.5) \times 10^{-3}$ V as the load varies in the experiments described above, it is neces-

sary that the ratio between the concentrations $\frac{[Me_{akt}^{n+}]}{[Me^{n^+}]}$

should be 1.1–1.2 times higher than the load increases in the process of friction. To control the chaotic autooscillations of tribo-EMF observed experimentally, the changes in the ratio of the potential-determining ions must be lower by an order of magnitude. The oscillations are determined both by metallic sol coagulation and by tribochemical complexing reactions on the friction surface and clustering processes in the contact zone when the servovit film appears during the existence of the wearless effect.

Therefore, given the results in [9], it can be assumed that the appearance of the servovit film in the copperalloy–glycerin–steel tribosystem occurs according to the same mechanism as in tribosystems of the steel– metal-cladding–lubricant with copper nanonparticles type, introduced beforehand [12]. In other words, the time required for the copper-alloy–glycerin–steel tribosystem to transit to the wearless mode can be dictated by the accumulation of copper clusters of the proper dimensions and concentration, that participate in the servovit film formation.

Analysis of the data of tribochemical [13], including triboelecrochemical [2, 3], reactions in classic copperalloy-glycerin-steel tribosystems leads to the conclusion that the wearlessness effect is governed by the evolution of the processes of tribocoordination and triboreducing decomposition of the copper complex [13], as well as the processes of metallic copper triboclustering [14] in the friction zone. Thus, copper-containing complexes are definitely present in the lubricating material when self-organization and the wearlessness effect occur. These complexes include both copper coordination compounds and their nanodimensional clusters, with the ratio between them dependent on the friction conditions and the composition of the lubricating medium. Specifically, these products, copper nanoclusters in particular, ensure the formation of a servovit film with a unique nanocrystalline structure and unprecedented triboengineering characteristics.



Fig. 3. AFM image of copper clusters obtained during friction in water–glycerin mixture (nominal pressure 10 MPa, sliding velocity 1 m/s).

A hypothetical molecular mechanism of servovit film formation and origination of auto-oscillations in self-organizing tribosystems was advanced earlier based on the results of study of the self-organization molecular mechanism in friction in works [12, 15–20] and [18] in particular. The essence of the proposed mechanism is that periodic oscillations of the force of friction and sizes of rubbing bodies result from the stepwise process of sol coagulation in the friction zone, while the gradient of electrolyte concentration resulting from the coagulation of clusters is a governing parameter determining the mechanism of appearance of autooscillations and self-organization in the tribosystems in question. Hence, investigation of the structure of copper nanoclusters is essential both to explain the mechanism of their coagulation on the friction surface and to reveal how the triboengineering properties relate to the nanostructure of the servovit film.

Investigation of the copper clusters with the AFM method under conditions simulating frictional interaction (Fig. 3) shows that the clusters precipitated during formation of the servovit film are stacks of nanosized copper wafers each about 100 nm thick that may be separated by an external power effect (Fig. 4).

The laminar structure of the clusters appearing in friction, at the initial stage of self-organization during wearlessness, allows us to explain the merging antifrictional effect by the slight sliding of the wafers in the stack separated by a lubricating layer similar to that observed by A.S. Akhmatov [21] during abnormally low friction when investigating the mechanical properties of boundary lubrication on the steel mirror surfaces (the stack method).

In this case, the external loading produces a condensate crystalline structure in the precipitated laminar clusters that favors release of a much larger amount of the electrolyte into the lubricating medium than occurs when the condensed crystalline structure appears from the usual sol colloid sediments. The appearing concentration gradient normal to the friction surface appar-



Fig. 4. AFM image of copper clusters in Fig. 3 after exposure to ultrasound in isopropyl alcohol at frequency 35 kHz and power 60 W for 5 hours.

ently stabilizes the auto-oscillations, including the tribo-EMF oscillations in the self-organizing tribosystems treated in the present work.

The data on the tribo-EMF variations during the evolution of the self-organizing tribosystems studied in the current paper allow us to perform simple estimates of the energy of electrolyte adsorption on the clusters using the equations of relaxation time τ when the steady state is upset during coagulation. In fact, assuming that the equilibrium of adsorption \leftrightarrow desorption is considerably shifted towards adsorption (which is the condition necessary for coagulation) and the electrolyte adsorption on the clusters can be considered as a reversible chemical reaction

$$\begin{array}{c} \kappa^{\leftarrow} \\ K + \varepsilon \longleftrightarrow K\varepsilon, \\ \kappa^{\rightarrow} \end{array}$$

where *K* is the clusters; ε is the electrolyte adsorbed on its surface; $K\varepsilon$ is the cluster with the adsorbed electrolyte; κ^{\rightarrow} and κ^{\leftarrow} are the constants of the rates of adsorption and desorption, respectively; and, in accordance with [22], the equation of relaxation time τ can be recorded in the following manner:

$$\frac{1}{\tau} = \kappa^{\rightarrow}[\varepsilon] + \kappa^{\leftarrow}.$$

Approximately, disregarding the desorption, we obtain

$$\frac{1}{\tau} = \kappa^{\rightarrow}[\varepsilon].$$

Here, $[\varepsilon]$ is the equilibrium electrolyte concentration in the lubricating layer in the clearance between the bodies. In this case, the relaxation time τ can be considered as a period of small oscillations induced by the appearance of nonspontaneous tribo-EMF.

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Assuming that the concentration [ɛ] depends only

depends on the temperature *T* similarly to the value κ^{\rightarrow} (i.e., it follows the Arrhenius equation

slightly on the temperature and that the value

$$\frac{1}{\tau} = A \exp\left(-\frac{E_a}{RT}\right),$$

where E_a is the energy of adsorption activation), we obtain graphically (Fig. 5) the value of the latter for the bronze–butanediol–1,4–steel tribosystem from the equation

$$\ln\frac{1}{\tau} = \ln A - \frac{E_a}{R}\frac{1}{T}.$$

The presented data show a linear dependence (with the coefficient of correlation 0.993) of the inverse relaxation time logarithm on the inverse temperature; this allows us to obtain the value $E_a = 46.5$ kJ/mole of butanediol-1,4 on the copper surface. The obtained energy of adsorption activation can be compared with the enthalpy of adsorption bearing in mind that the activation barriers are usually higher than the enthalpy process [22]. This result shows that the process energy corresponds to the energy of physical adsorption (up to 80 kJ/mole) [23].

CONCLUSIONS

An experimentally justified molecular mechanism is proposed to explain the triboEMF auto-oscillations in the steel-copper-alloy friction pair based on the assumption of periodic coagulation of copper nanoclusters on the friction surfaces. The mechanism favors the formation of nanosized servovit film structure during self-organization of tribosystems under the wearlessness effect.

It is shown that the governing parameter of tribo-EMF oscillations is quick change in the electrolyte concentration under load (the electrolyte penetrates into the contact zone) applied to the stack of nanosized metallic wafers forming the servovit film in the lubricating layers directly underlying the contact surface.

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DESIGNATIONS

V—sliding velocity; *T*—temperature; ΔE_{spon} —the galvanic element EMF resulting from the spontaneous process; ΔE_0 —the standard EMF of this element; $[\text{Me}_{akt}^{n+}]$ —the concentration of cations of the more active metal in the anode space; $[\text{Me}^{n+}]$ —the concentration of cations of the less active metal in the cathode space; *n*—the valence of cations; *R*—the universal gas constant; *F*—the Faraday number; $\Delta E_{\text{non-spon}}$ —the con-tribution of the friction-initiated nonspontaneous pro-



Fig. 5. Estimates of $1/\tau$ values in response to temperature of bronze –butandiol-1,4–steel tribosystem.

cess into the tribo-EMF; ΔE —the total tribo-EMF; *K*—cluster; ϵ —the electrolyte adsorbed on its surface; *K* ϵ —the cluster with the adsorbed electrolyte; κ^{\rightarrow} and κ^{\leftarrow} —constants of the rates of adsorption and desorption, respectively; τ —the relaxation time when the steady state is upset during coagulation; [ϵ]—the equilibrium electrolyte concentration in the lubricating layer in the gap between the bodies; E_a —the energy of adsorption activation.

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