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DERIVATION PROCESSES OF FLUORINE-CONTAINING WEAR INHIBITORS OF METAL-POLYMER SYSTEMS

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Abstract

This article presents the formation mechanisms of separation layers formed by wear products of metal-polymer tribological systems components. It is shown that these formation mechanisms determine work and kinetics of separation layers frictional interaction. Using the barrier model was justified the formation of ″charge mosaic" on counter-surface of tribological system. This mosaic leads to the formation of local transfer areas followed by their transforming into a stable separation layer that defines mechanisms of friction and wear.

Keywords: inhibitor, frictional interaction, friction surface, tribosystem, barrier model, energy state, charge mosaic.

1. Introduction

According of low wear tribological system concept created by, leading role belongs to wear inhibitors – components introduced into the tribological system from outside or formed as a result of tribochemical reactions promoted a suppression of adverse conversion cycle which intensifies processes of wear.

In any kinds of contact interaction in different composition and a design tribological systems are formed layers that act as anti-wear component. One of the most important task of tribological engineering is support of such layers formation conditions with parameters necessary and sufficient for the stable maintenance of friction unit during specified life.The solution of this problem is based on system analysis of features of the tribochemical transformations of the tribological system components in certain operating conditions, detection of prevalent contact reactions cycles determined wear and selection of effective methods of control them via constructive, technological, material science solutions.

The choice of a particular type of wear inhibitor determined the compatibility of friction pair components, therefore the most optimal servicing mode of the friction pair, involves analysis of various types of operating conditions realization for specified servicing modes.

In this regard, the investigation of influence of the tribological system components energy state on the mechanism and kinetics of the formation of separation layers in the area of bearing and shaft frictional contact has a significant scientific and practical interest. The structure and stability of these separation layers define parameters of tribological characteristics of friction pair.

2. Methods

It is known that frictional interaction of metal-polymer tribological system components – shaft and bearing – is accompanied by wear particles transfer phenomena and formation of the separation layer whose composition and structure depend on using materials and operating conditions of the friction unit. Using the directional control of physical and chemical processes in the contact area, it is possible to create conditions for the prevailing formation of products that will reduce friction and increase wear resistance of the friction unit, or in other words, will perform function of the component reduced the wear rate – wear inhibitor.

The thin films of fluorine-containing components of different molecular weight, structure and production technique are rated among the effective wear inhibitors of "metal-metal" and "metal-polymer" systems. It has been found that irrespective of structure and mass, films of fluorine-containing oligomers coated from solutions, formed from the active gas phase, rotaprint thin films from products of thermogas dynamic synthesis (TGD-synthesis) of polytetrafluoroethylene, transfer thin films of the wear products of polytetrafluoroethylene and composites are effectively reduce wear of tribological systems operated without external supply of lubricant or lubricated by oils and plastic compositions based on oil and synthetic products.

In spite of this type of wear inhibitors formation technologies differences, probably, there are general prerequisites for the realization of their beneficial effect on tribological processes due to structural features of thin films on solid substrates of various composition. It is seen that significant role in structural and phase transformations of thin-film fluorine-containing wear inhibitors are played energy characteristics of the metallic counter-surface that is represents a complex heterogeneous system.

An obvious consequence of the heterogeneous structure of the metal components is nonequilibriumof charges transfer processes between the individual areas of the surface layer and the interface of static and dynamic metal-polymer systems components that have a significant impact on contact processes, especially on the mechanism and kinetics of mechanochemical wear.

In connection with this, significant interest is analysis of metal components structure features in terms of the charge state of the metal substrate surface layer.

Hamiltonian of independent electron model (adiabatic approximation) in the Schrodinger equation,isgivenby Eq. (1):

$$\hat{H} = -\frac{\hbar^2}{2m}\Delta + u(\vec{r}), \tag{1}$$

Where ħ is the Planck constant, m is the electron rest mass, $u(\vec{r})$ is the potential function.

If the Hamiltonian (1) is used to describe the state of an electron in the crystal, that is in the field of periodic potential, that $u(\vec{r})$ has view as Eq. (2)

$$u(\vec{r}) = u(\vec{r} + \vec{R}), \tag{2}$$

where $\vec{R}$ is a translation vector which equal Eq. (3)

$$\vec{R} = m\vec{a} + n\vec{b} + p\vec{c}\ , \tag{3}$$

where $\vec{a}$, $\vec{b}$, $\vec{c}$ are the Bravais lattice, m, n, p are integers.

A solution to the Schrodinger equation for adiabatic approximation with a periodic potential is the wave functions, defined by the Bloch Theorem stated in is given by Eq. (4):

$$\psi_{nk}(\vec{r}) = \varphi_{nk}(\vec{r}) \cdot \exp i\vec{k}\vec{r}\ , \tag{4}$$

where the wave vector $\vec{k} = 2\pi\vec{s}$, $\vec{s}$ is the reciprocal lattice vector. The function $\varphi_{nk}(\vec{r})$ has the property of periodicity. According this we have Eq. (5)

$$\varphi_{nk}(\vec{r} + \vec{R}) = \varphi_{nk}(\vec{r})\,. \tag{5}$$

Inserting solutions of the form given in Eq.(1-5), we get Eq. (6):

$$\psi_{nk}(\vec{r} + \vec{R}) = \varphi_{nk}(\vec{r} + \vec{R}) \cdot \exp ik(\vec{r} + \vec{R}) = \varphi_{nk}(\vec{r}) \exp ik\vec{r} \cdot \exp ik\vec{R} = \psi_{kk}(\vec{r}) \cdot \exp ik\vec{R} \tag{6}$$

The received Eq. (7)

$$\psi_{nk}\left(\vec{r}+\vec{R}\right)=e^{ik\vec{R}}\cdot\psi_{nk}\left(\vec{r}\right) \tag{7}$$

is another form of the Bloch theorem [12].

One can see from the Eq. 7 that the wave function of an electron in a periodic potential field $(u(\vec{r}))$ corresponds to the solution of the Schrodinger equation for a free electron $(\psi(\vec{r}))_f$

$$[\psi_k(\vec{r})]_f=\psi_0\exp\left(i\vec{k}\vec{r}\right), \tag{8}$$

but instead of a constant amplitude factor ψ_0 in the equation 7 is the wave function with period R. The wave number (k)is called the zone number. For a fixed(k) there are many independent own states with their specific energy values, which are distributed to zones, separated by energy values that are not eigenvalues of the Hamiltonian, that is prohibited for electronic states.

In attempting todescribe the state of an electron near the surface of the crystal it should be appreciated that in these areas of the substance is breached the periodicity of potential and on the surface of crystal is created the so-called surface barrier, whose shape depends on many factors, beginning with defects of different nature (by the way, the surface itself is two-dimensional defect), also with the surface layers morphology. The function of the surface potential (u_s) changes its shape in passing from one point of the surface to another, that is

$$u_s=u\left(\vec{Q}\right), \tag{9}$$

where $\vec{Q}$ is the position vector of a point on the surface.

In this work it's shown that under the breach of periodicity of potential near the surface the wave function takes the form different from those given by equations 5 and 9.

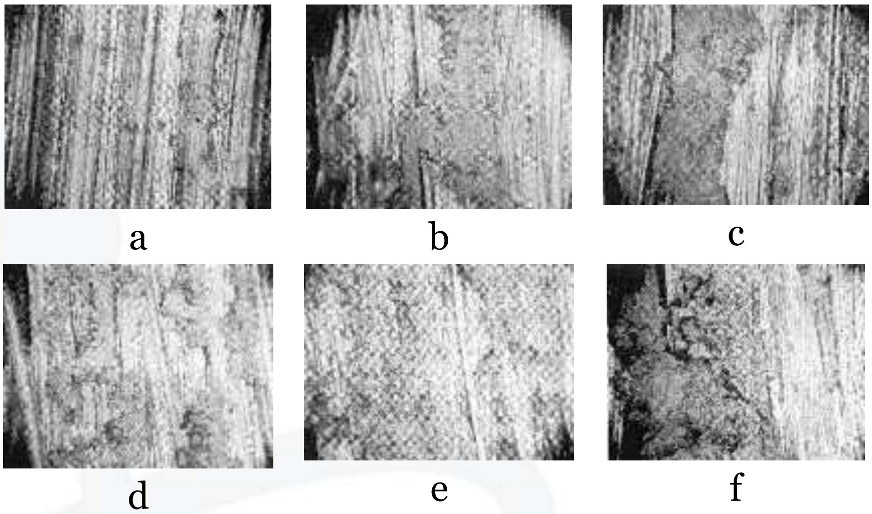
Note that the function ψ falls off exponentially outside of metal and has an exponentially decreasing envelope inside. In this case, along with real wave vectors $\vec{k}$ inside the crystal there are other solutions with the complex wave vectors that correspond to states of electrons localized near the crystal surface different from the bulk. These surface states with specific energy levels have been considered for the first time by I.Y. Tamm and bear his name – Tamm levels.

In discussing of the crystal bulk properties the influence of these surfaces layers are neglected, because that the ratio of the surface levels number to Bloch levels not exceeding ratio of the surface atoms number to the total atoms number in a crystal, which for the macroscopic prototype does not exceed 10^{-8}.

3. Results and Discussion

As a result, surface levels give disparagingly small contribution to the bulk properties; the exception is nano-objects whose surface and dimensional factors play an important and often main role. However, in single crystal the Tamm levels are also very important for the determining of crystal surface structure. For example, they should be considered in any microscopic calculation of the surface layer structure.

The frictional interaction of the components metal-polymer tribological system causes the formation on contact surfaces the layer with specific morphology (Fig. 1). The fixation of wear particles of the model sample manufactured by compression of graphite particles with a size of 1-5 micrometer is a result of the energy (charge) and morphology (size) factors cumulative effect. This is evidenced by the specific structure of the transferred layer, whose area depends on the number of cycles of frictional interaction tribological system components (Fig. 1, b-f).



a b c

d e f

Figure 1 – The morphology of the surface layer of the sample made of steel 45 after frictional interaction with a graphite sample: a – the original; b – after 10 cycles; c – after 20 cycles; d – after 30 cycles; e – after 40 cycles; f – after 50 cycles

The unstable character of the formation process of the separation layer leads to breakdown in process of stable operation of a particular friction unit that may be lead to its failure in the presence of regime excursions caused by a combination of factors – physical, organizational, qualifications, etc.

An effective way to increase parameters of the service life and reliability of tribological systems is the using of special methods to increase of the spacer layers stability via selection of components for composition, preparation technology of friction union surfaces, directional control of mechanisms and kinetics of favorable cycles of tribochemical reactions. It is obvious that in choosing these methods is very important to take account of energetic features of materials formed wear inhibitors, which are due to their composition, crystal-chemical structure, defectiveness and others factors.

The effective wear inhibitors of metal-polymer tribological systems are thin-film coatings formed by solution and vacuum technologies. It is known that coating the friction surface by thin films of fluorinated oligomers such as "Epilam", "Foleoks" [8] and the formation of films by nitrides and carbides of titanium (TiN, TiC, TiCN, etc.) provides increase of various design friction couples wear resistance.
Multivariate mechanism of inhibitory action of these thin films is also determined by the energy state of the metal substrate on which they are formed.
The action mechanism of fluorine-containing high-molecular components thin-film coatings with using of various techniques (solution, rotaprint, vacuum, mechanochemical) has plenty going for the common control methods of energy and morphological parameters of metal-polymer system elements, because it provides highly efficient of inhibitory effect on the wear process, does not require using of special machine-tool attachments (sand wheel blasting, phosphatization, etc.) and can be used in precision friction units.
The presence of fluorine-containing high-molecular compounds sublayer helps to reduce the running-in time of friction unit and to the formation of separation (transferred) layer with a specific surface area W = 0,85 ÷ 0,95 of the total area of friction surface (Fig. 2).

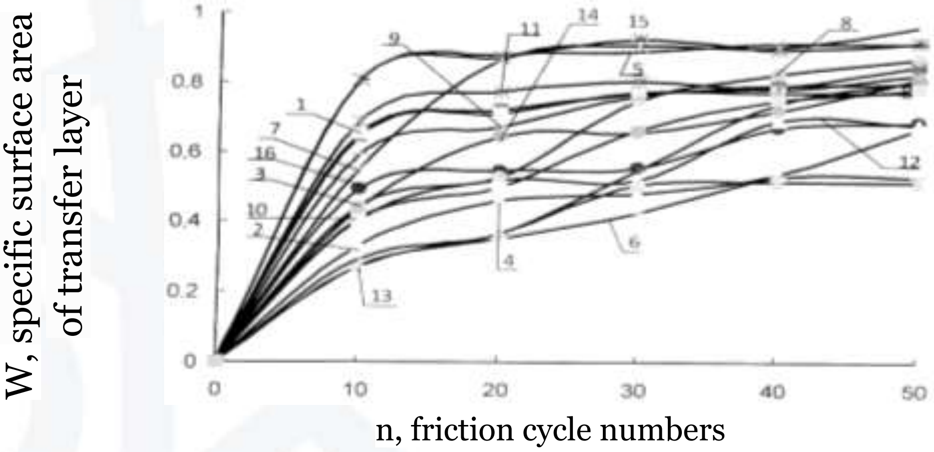


Figure 2 – The kinetics of mass transfer for friction process of the carbon sample with various surface pre-treatment counterbody: 1 – TiN + F-1; 2 – phosphate layer (5min) + F-14; 3 – phosphate layer (15 min) + F-1; 4 – TiN + F-14; 5 – TiN (dropping phase) + F-1; 6 – phosphate layer (15 min) + F-14; 7 – steel 45 + sandblasting + F-1; 8 – steel 45 + sandblasting + F-14; 9 –TiN (dropping phase) + F-14; 10 – phosphate layer (30 min) + F-14; 11 – phosphate layer (30 min) + F-1; 12 –steel 45 + F-14; 13 –steel 45 + F-1; 14 – phosphate layer (5min) + F-1 + F-14; 15 – phosphate layer (5min) + F-1; 16 – TiN + F-1+ F-14

Thus, taking the energy and morphological factors into account for choosing of the composition and components application technology, which provide the inhibitor effect of the metal-polymer tribological system wear process, determines attainment of the service life and reliability high parameters.

4. Conclusion

Energy state of the surface layer of the metal-polymer tribological system metal component characterized by the presence of a charge mosaic determines necessity for the using of special components for the formation of the separation layer with high stability. As componentsfor the formation of wear inhibitorsare effective the fluorine-containingpolymer and oligomer compounds coated by solution, rotaprint or vacuum techniques.

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