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## INFLUENCE OF ACTIVITY OF LUBRICANT MEDIUM ON TRIBOCHEMICAL ENDURANCE OF COMPOSITION COVERAGES

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*The influence of activity of lubricant medium on tribochemical endurance of composition coverages in the condition of changing velocity of slide and loading is researched.*

At the presence of lubricant medium the serviceability of friction units of details of machines is defined by a condition of lubrication. Most unfavorable and dangerous for loaded kinematics friction pairs there is a work in the conditions of boundary lubrication [1]. The boundary lubrication is the least designed partition of a common problem of lubrication of machines in connection with complexity of the phenomena, enveloped by it, first of all such, as absorption, chemical absorption and chemical processes, plastic deformation and activation process of surfaces, energy interactions at friction and others [2; 3].

The boundary friction, especially at the presence of a mass with reactive by the components, is accompanied by formation of modified stratum, this why one of primal problems, defining operation opportunities of the tribological system as a whole, is the examination both control by a composition and properties of surface layers.

The modern introducing of mechanisms of anti-friction and non-wear operation of heterogeneous coverages in the requirements of boundary friction carry individual character and did not rest on due experimental affirming. The doubtless interest represents examination of dependences of a friction coefficient and intensity of wear from an aspect of lubricant materials and fissile components, surface layers and tribological processes, and also power and kinematics requirements in a contact band.

The executed examinations are guided on disclosing of regularities of wear of heterogeneous coverages at maintenance in different lubricant mediums, the clearing up of the mechanism of influence of surface active substances on intensity of wear, friction coefficient and load-velocity gamut, installation of areas of inconvertible development of the structural adaptation effect.

The processes of friction and wear of heterogeneous coverages in an inactive lubrication (liquid petrolatum) and in the same lubrication, but labia-

lized by the components of surface-active substances were investigated.

The wear tests were carried out by the special friction machine UMT at regular feeding of lubrication in a band of contact of friction parts (DXd=25X17.5). The width of coverages after operational development was 0,18 – 0,20 mm, surface roughness  $Ra = 0,63-0,32$ .

In requirements of boundary lubrication the composition of heterogeneous coverages on the basis of nickel (Ni, Al, Si), on the basis of iron (Fe, Ni, Cr, Al, B) and on the basis of a carbide of chrome ( $Cr_3C_2$ , Ni, Cr) were tested. The samples of contraparts were made from widely used materials such as 30XГCA, 38XMIOA, steel 45, Br014, AO-20; as lubricant mediums we used: liquid petrolatum, liquid petrolatum with the components of a surface-active substance (2 % of oleinic acid); the mineral oil MC-20 with consequent differentiated introduction sulfuric, chlorine and phosphorus addition agents; motor oil M-10G2 synthetic oil – B-3B.

The selection of an inactive lubricant medium alongside with oils containing a surface-active substances and an addition agent, is interlinked to clearing up of the basic processes and regularities of mechanisms of wear of composition heterogeneous coverages in requirements of boundary friction and with examination of influence of addition agents to a kinetics of formation of secondary structures with those or other properties.

With the purpose of study of the influence of doping elements on processes of friction of three-component heterogeneous coverages on the basis of nickel with the components Al, Si, their structure both in an initial state, and after the wear tests was explored.

The accomplishing of X-ray phase analysis of coverages of system Ni-Al-Si has considerable difficulties, because that many lines of different phases are superimposed against each other, the presence of internal stresses gives in their expansion, and the

high speeds of cooling at forming a coverage promote formation of amorphous structures. For an estimation of a phase composition of coverages the comprehensive approach with application of the X-ray diffraction and metallographic analysis utilized.

Agrees of constitution diagrams of systems Ni–Al, Ni–Si in structure of a coverage, plotted by a composition dust Ni–Al–Si, there can be following phase components: solid solutions Ni in Al, Ni in NiAl, Ni in Ni<sub>3</sub>Al, Si in Ni<sub>3</sub>Al, Al in Ni, Si in Ni, and as intermetallic compounds: NiAl; Ni<sub>3</sub>Al; Ni<sub>2</sub>Al<sub>3</sub>. Besides at a spraying in mediums oxygen-bearing, there should be oxides of nickel, aluminum, silicon which is generatrix at a spraying. It is necessary, however, to take into account, that the high speeds of cooling at forming of a coverage can go to the formation stable metal phases such as Ni<sub>2</sub>Al<sub>3</sub>.

The X-ray phase and the metallographic analysis of an initial state of coverages (before friction tests) has shown, that the reference feature of a microstructure is multiphase and shallow dispersibility. On X-ray patterns of such coverages there are lines of phases Ni<sub>3</sub>Al and NiSi, and also oxides Al<sub>2</sub>O<sub>3</sub>, NiO, SiO<sub>2</sub>, and on the base of intensities of lines it is possible to mark, that quantity of phase Ni<sub>3</sub>Al in percentage more, than the quantity of phase NiSi.

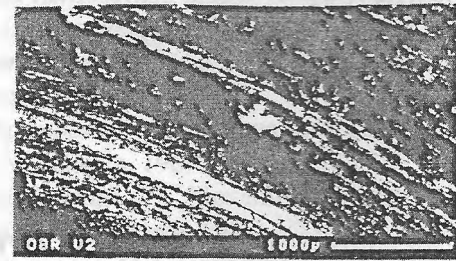
The padding metallurgical surveys have allowed to place that there is a free silicon in a composition of a coverage, which has not reacting with nickel, as separate inserts.

After a trial of coverages in requirements of boundary lubrication, a microstructure and phase composition of a friction surface have varied a little. On X-ray patterns of such coverages the intensity of a line of a phase Ni<sub>3</sub>Al is considerably reduced, there are lines of phases Ni<sub>2</sub>Al<sub>3</sub>, Ni<sub>2</sub>Si,  $\delta$ -Ni<sub>2</sub>Si.

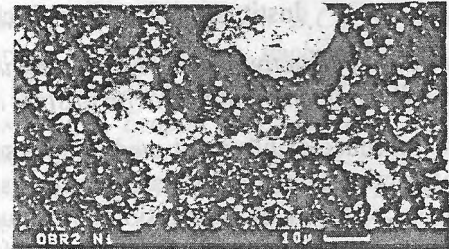
By padding metallurgical surveys the presence of free silicon on a friction surface is not revealed. It means, that during the friction on both contacts there are structural transmutations to formation of new phases. Free and unreacted during the manufacturing and spraying silicon forms a solid solution Si in Ni<sub>3</sub>Al. At the expense of it the content of a phase Ni<sub>3</sub>Al is diminished and there are new finely divided phases Ni<sub>2</sub>Si,  $\delta$ -Ni<sub>2</sub>Si.

Simultaneously, local heat-up on spots of actual contact and fast cooling after escaping from it create conditions for formation of a metal stable phase Ni<sub>2</sub>Al<sub>3</sub>. Besides the occurrence of finely divided high-melting phases considerably changes structure of a nickeliferous matrix, ensuring considerable hardening.

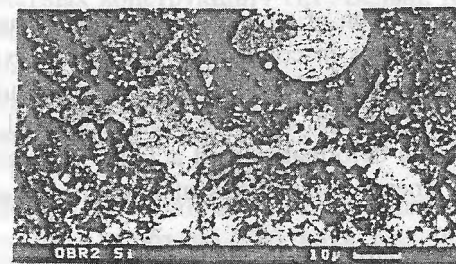
The finely divided and heterogeneous structure of coverages prove to be confirmed by the examinations executed on the microanalyzer. In a fig. 1 the



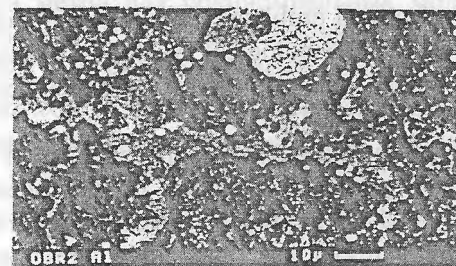
a



b



c



d

Fig 1. Microphotos of a friction surface of a coverage and allocation of bands of localization Ni, Si, Al in microvolumes of surface layer:  
a – the microphoto of a friction surface of a coverage;  
b – allocation of Ni; c – allocation of Si; d – allocation of Al

microphotos of some structural features of allocation of builders of coverages working in requirements of lubrication are submitted.

For affirming the phenomenon of segregation of doping elements with reference to a friction surface both the deriving of quantitative and qualitative estimations of the content of aluminum and silicon on a friction surface examinations with application of an auger-spectroscopy were carried out.

The auger spectra which have been taken off immediately from a friction surface (I) and after an

ionic etching up to depth 5000 Å (2) show that, the chemical composition of a friction surface and under surface layer considerably differs, the spectrum (1) is considerably transformed in relation to a spectrum (2), except for a basic element on a friction surface, nickel, aluminum, silicon, oxygen, phosphorus, sulfur, chlorine and carbon.

The quantitative analysis of the content of numbered devices on a surface submitted in the table.

**Quantitative analysis of allocation of chemical elements**

Chemical elements	The friction surface, %	Depth 5000 F, %	Material matrix
P	5,4	1,8	–
S	6,4	1,4	–
Cl	1,5	0,4	–
C	23,8	26,4	4,3
Ni	30,8	32,1	83,4
Al	16,4	22,6	7,5
Si	10,8	15,0	4,8

At a level-by-level ionic etching of a material with a simultaneous chemical analysis the regularity of allocation of chemical elements was established. The qualitative pattern of allocation of chemical elements on depth of an etching was made up.

From introduced results follows, that the doping devices during abrasion segregate to a surface of a material. However, the maximal content of aluminum and silicon is revealed in a subsurface stratum, on depth up to 5000 Å, which exceeds in three times the content in a matrix of a material. Oxygen behaves in a similar way. Its presence can be explained by diffuses of aluminum and silicon in the field of segregation, forming diffusive sites consisting of oxides.

With reference to the auger-spectroscopy was having analyzed allocation of a coverage, included in a composition, of doping elements of aluminum and silicon at operation of a coverage in lubricant mediums phosphoric, sulfuric, chloral addition agent. The carried out analysis has shown, that aluminum and silicon diffuse from volume of a material to surface and subsurface stratum. In surface layer is: aluminum – about 17 %; silicon – about 8 % (depending on a condition of friction), in a subsurface stratum their content is augmented up to 20 and 10% accordingly.

Thus it is necessary to mark, that the allocation of oxygen on depth of a coverage has the same character, as allocation of aluminum and silicon. Thus the maximal content of phosphorus, sulfur, chlorine in basic recorded on a friction surface and is promptly diminished on depth of an etching. On all visibility,

these elements diffused from lubricant medium, since. In a matrix of a material their presence registered on a hum level. The presence of oxygen in a matrix of a material is explained by an oxidation of aluminum and silicon contained in particles of a dust, during a spraying.

At influence of surface-active substances on regularity of friction and wear of heterogeneous coverages as lubricant medium was utilized both pure (non-polar) liquid petrolatum, and liquid petrolatum with the component 2 % oil of monobasic unsaturated oleinic acid. Optimum density of oleinic acid discovered experimentally, thus an estimation of lubricant properties defined on magnitude of a friction coefficient. It was established, that in accordance with a heightening of the content of oleinic acid up to 2 %, the magnitude of a friction coefficient, being diminished, achieved a fixed level, on which remained stable down to density of an one-oxide acid relevant almost 45 % oil.

Thus, the optimum density of oleinic acid in liquid petrolatum relevant to minimization of parameters of friction, has made 2 % oil. Besides for the comparison of obtained results the similar pairs of friction under the same programs tested in medium of mineral oil MC-20.

The results of examination, at a test of coverages in medium of liquid petrolatum, in which do not contain surface-active substances the minimum magnitude of a wear is observed at the maximal friction coefficient. At adding surface-active substances in liquid petrolatum the intensity of wear is augmented almost twice at simultaneous lowering of a friction coefficient.

Thus it is necessary to mark, that the gamut of the normal wear on a loading at a lubricant operation of liquid petrolatum rather low, up to 8 MPa, and it is considerably dilated at introduction of surface-active substances – up to 13 MPa. The noticeable lowering of the coefficient of friction and magnification of a stability boundary, defining gamut of maintenance, is interlinked to a chemisorptions of oxygen on a friction surface and formations of protective secondary structures of oxides, and also with effect of physically adsorbed surface-active substances stipulating the plasticizing.

The magnification of a loading renders more effective influence, than the heightening of velocity of slide, that, radiating from development of a Rehbinder effect, is interlinked to a nonequilibrium labialized state of surface layer and structure, oriented during friction. The liquid petrolatum containing in the composition surface-active substances, adsorbed on surfaces of a coverage, deformable at friction, calls the adsorption plasticizing, and etc.

The ability to more intensive strain (slide goes on many systems of crystallographic planes) in thin surface layer by width in shares of a micrometer, thus the surface-active substances facilitate to an exit of dislocations to a surface of a deformable coverage, that diminish internal stress and prevents distribution of a strain deep into is model.

In a fig. 2 the changes of dislocation structure are shown at friction in medium of liquid petrolatum (*a*) and in requirements of lubrication with adding of surface-active substances (*b*).



Fig. 2. Dislocation structure of a coverage on the basis of nickel:

*a* – at friction in medium of liquid petrolatum; *b* – at a friction in requirements of lubrication with adding of surface-active substances

The simplification of sliding at the presence of surface-active substances eventually gives in considerable hardening of thin surface layer owing to strong contortions of a lattice. The changes of lattice constants under influence of loadings, temperatures, reverting and phase changes do not flow past uniformly because of localization of strains in separate volumes, commensurable with sites of actual contact, thus the central volumes of particles with a distortionless crystal lattice less strong and have smaller strain resistance, being by potential cold-welded regions, and the area, near to the boundaries of grains or to sites with a garbled crystal lattice, appear by stronger. This localization also stipulates the dissimilarity of mechanical characteristics, definiendums by a regression to an average level on friction surfaces of coverages. For the analysis of the processes the allocation of the microhardness from a friction surface on depth of a deformed stratum is obviously important.

The results of measuring of the microhardness on depth of a deformable stratum for three lubricant mediums executed on a procedure are submitted [2]. A point relevant to a microhardness  $H\eta = 3700$  MPa, characterizes a microhardness of an initial sample up to the friction test.

At operation in liquid petrolatum the microhardness of surface layer raises insignificantly, up to  $H\eta = 5880$  MPa, thus the depth of a deformable band achieves a considerable magnitude

$h = 1,78$  microns. Adding in liquid petrolatum of surface-active substances essentially raises a microhardness of a friction surface  $H\eta = 14500$  MPa, at simultaneous diminution of depth of a deformable stratum  $h = 1,14$  microns. The results, obtained at friction in medium of oil MC-20, occupies an intermediate position. On the base of results it is necessary to mark, that the degree of the originating reverting at deformation of a surface of a coverage considerably increases at the presence of surface-active substances, i.e. the microhardness of a hammer-hardened stratum raises, that essentially influences on antifriction property of a coverage and, as it is known promotes magnification of a yield strength of a material of surface layer, and, hence, to expansion of a gamut of normal outwearing both on a loading, and on velocity of slide. Above-stated takes place at Rehbinder effect, which is shown at operation of coverages in medium containing a surface-active substances. It, first of all, also explains the considerable magnification of a load-velocity gamut of operation of a coverage as contrasted to by lubricant medium which is not containing of surface-active substances.

However presence of surface-active substances at friction of detonation coverages calls undesirable competing processes, so is simultaneous with Rehbinder's effect the interior effect is shown [4], which takes place during an adsorption of surface-active substances on interior surfaces of pores playing a role of germs of crazes. It goes to the lowering of the energy that expended on formation of new surfaces and to the simplification of a development of cracks, that is shown in a heightening of a brittleness and sharp magnification of wear of coverages.

The inverse relation is observed at change of a friction coefficient, the maximal value of a friction coefficient corresponds to liquid petrolatum, minimum – oil MC-20, that first of all, it is possible to explain not only because of the presence surface-active substances in MC-20, but also by its good adsorption to a friction surface for the score of higher kinetic viscosity as contrasted to by liquid petrolatum.

As have shown the carried out experimental examinations, the surface-active substances render considerable influence on process of friction and wear of heterogeneous coverages. At the absence of surface-active substances in lubrication the minimum wear is observed at an inappreciable load-velocity gamut and high friction coefficient, the adding in lubricant oil of surface-active substances considerably dilates a load-velocity gamut, reduces a friction coefficient, but thus the wear as is augmented, a simultaneous operation of interior and exterior Rehbinder effects in this case takes place.

Utilizing reduced results about an the operation of interior and exterior Rehbinder effects during boundary lubrication, it is possible to assume the following wear mechanism of heterogeneous coverages at presence of lubricant medium. During the contact an interaction occurs not only strain of surface layers, grains, but also change of their orientation, i.e. texturing. In other words, the friction surface adapts to the operating scheme of mechanical efforts. That is visible in microphotos of friction surfaces (fig. 3), relevant to different conditions.

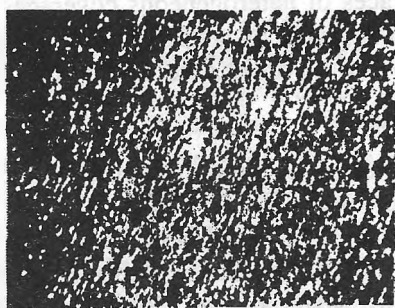


Fig. 3. Microphotos, that illustrate the texturing of friction surfaces of heterogeneous coverage's relevant to different conditions (x320)

The presence of surface-active substances by means of appearance of an exterior Rehbinder effect on a friction surface promotes the forming of structures, which stipulate the adapting phenomenon. If the strength at friction does not exceed the yield strength of a material, which depends on the size of meshes, a normal wear takes place, if the strength at friction becomes more than the yield strength of a material, there is a fracture, thus of a wall of meshes oriented perpendicularly to a direction of friction, initiate a beginning of fracture, since are concentrators of strengths and radiants of cracks.

Simultaneously at operation of such material, as the heterogeneous coverage containing high-melting phases, the formation of microemptinesses in a sub-surface stratum will occur, and the presence of an inappreciable porosity in a material at a simultaneous operation of an interior Rehbinder effect promotes disclosing of emptinesses and cracks, that goes to the formation of dusts of wear.

Analyzing explained above, it is possible to make an output, that at friction of heterogeneous coverages at presence of lubricant medium the important role will play presence of surface-active substances in lubrication, which stipulate development of different aspects of a Rehbinder effect and determine the mechanism of wear of the material.

At holding experiences on definition of a degree of influence of element-organic addition agents on processes of friction and wear of coverages as base,

the oil MC-20 was selected, in which differentiated element-organic addition agents were added: phosphoric – three-crezilphosphate; sulfuric – free sulfur; chloral – benzyl chloride. The content of free sulfur in oil has made 0,25 % of masses, phosphorus and chlorine of masses, containing up to 1 %. The opportunity of application of the addition agents listed above at the lubrication of heterogeneous coverages requires a more detailed study.

As the carried out examinations show organic compounds of phosphorus, of sulfur and chlorine have good anti-score and anti-wear properties and are capable to organize on friction surfaces a heterogeneous coverage of secondary structures defending from wear and seizing.

At lubrication of friction surfaces of a heterogeneous coverage of system Ni–Al–Si the greatest effect is ensured by the sulfuric additional agent, since it ensures a wide gamut of normal outwearing of inappreciable intensity.

The sulfuric addition agent creates a coverage of a film of sulfides on a friction surface, consisting from NiS, Ni<sub>3</sub>S<sub>3</sub>, Al<sub>2</sub>S<sub>3</sub>, SiS<sub>2</sub> (to install a precisely phase composition of secondary structures it was not possible because of inappreciable width), distinguished by rather high hardness, strength and melting point. However the solid film of sulfides has considerable resistance to detrusion, that stipulates the higher friction coefficient as contrasted to by other addition agents.

Taking into account, that sulfides are formed at, higher temperatures as contrasted to other addition agents [5], all positive effects at boundary friction are shown only at high loadings and velocities of slide, when temperature in a band of frictional contact considerably increases. It also was observed at holding examinations.

At inappreciable loadings and velocities of slide the application sulfuric addition agents is inefficient.

The phosphorus addition agent gives conversed effect on intensity of wear, friction coefficient and gamut of normal wear there is a phosphorus addition agent, as follows from experiment, is effective at inappreciable loadings and velocities of slide, hence, of phosphorus begins to react with a friction surface of a detonation coverage at low temperatures, forming thus of an effective films of secondary structures of types: NiP, NiP<sub>3</sub>, NiP<sub>2</sub>, AlP, which have good movability, ability to self-treatment of imperfections on a friction surface and making stratified structure. These films, as the examinations have shown, have good anti-wear properties and ensure rather low friction coefficients on light conditions of friction.

However at a heightening of loading or velocity of slide, the considerable heightening of temperature

in friction units accompanying by the appearance a lacquer is observed. It is possible to explain it by the following: phosphorus, as well as the aluminum, exothermically reacts with nickel (heat effect is close to effect at synthesis of intermetallids). The sectional circumstance considerably reduces a load-velocity gamut of a friction pair and consequently the application of lubrications with phosphorus addition agents in heavy loaded friction units is undesirable.

From explained it is visible, that the phosphorus addition agent at operation of heterogeneous coverages operates primarily in the field of inappreciable loadings and velocities of slide, and, hence, in basic at rather low temperatures therefore sectional class of addition agents cannot be considered as a resort of an effective guard of heterogeneous coverages from a score occurring at high temperatures.

The chloral addition agent which generate the film of chlorides on a friction surface of heterogeneous coverages, occupies an intermediate position in relation to phosphorus and sulfuric addition agents, the Chlorides are formed in basic at high temperatures [6], so the effective operation of this addition agent, as well as chamois, is shown in the field of high loadings and velocities of slide. However chlorides are melted at lower temperature, than sulfides, it and is reflected in a upper bound of serviceability of the chloral addition agent, which is lower than at sulfuric, but is higher, than at the phosphoric.

The estimation of influence of serially emitted motor oils containing a complex of addition agents, mineral oil M – 10G2 and synthetic oil – B-3B on intensity of wear, friction coefficient and weight-velocity gamut of heterogeneous coverages, as it comes from the analysis of the results, shows that the examined oils, into which composition the complex addition agents go into, considerably improve

tribological parameters, simultaneously reducing intensity of wear, friction coefficient and considerably dilating a gamut of normal wear on a loading in relation to base oil MC-20.

As follows from reduced examinations, the efficiency of used addition agents in test specifications with heterogeneous coverages is not the same and in a general view of the mechanism of their interaction is reduced to a combined effect of chemisorptions of oxygen and adsorption of surface-active substances on labialized friction surfaces. At lubrication of friction surfaces of heterogeneous coverages the greatest effect is given by a sulfuric addition agent, then in the downward order, chloric and phosphoric.

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В.В. Щепетов, В.В. Варюхно, В.М. Стадниченко, Л.В. Бурдюженко, А.Г. Довгаль

Вплив активності мастильного середовища на трибохімічну зносостійкість композиційних покриттів

Проаналізовано вплив активності мастильного середовища на трибохімічну зносостійкість композиційних покриттів під час зміни швидкості ковзання та питомого навантаження вузлів тертя авіаційної техніки.

В.В. Щепетов, В.В. Варюхно, В.Н. Стадниченко, Л.В. Бурдюженко, А.Г. Довгаль

Влияние смазочной среды на трибохимическую износостойкость композиционных покрытий

Проанализировано влияние активности смазочной среды на трибохимическую износостойкость композиционных покрытий при изменении скорости скольжения и удельной нагрузки в узлах трения авиационной техники.