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# Superlow Interaction in Layered Structures

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*Strictly as per the compliance and regulations of:*

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## I. Introduction

To improve the physical and mechanical characteristics of the surface layers of parts in order to increase the durability and reliability of used durable and anti-friction coatings applied by various methods. Surface properties used in modern engineering austenitic stainless steels and titanium alloys can be improved by application of multilayer wear-resistant and anti-friction coatings. As such coatings have been used transition metal compounds IY-YI of the periodic system (dichalcogenides, nitrides, carbides, oxides), applied vacuum ion-plasma methods. Having a range of features of the crystal structure and properties of high anisotropy in various crystallographic directions resulted in widespread use for these purposes dichalcogenides of transition metals. Very promising and has several advantages are vacuum ion-plasma methods of applying such coatings based on ion (cathode) sputtering. Development of the theory of managing the growth of coatings based on transition-metal dihalcogenides and their relationship with the technology application, explain the process of the formation of coatings with high tribological properties and mechanism of anti-friction properties, as well as comprehensive investigations of the crystal structure and physical properties of coatings are important scientific and technical challenge.

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## II. Subjects and Methods

Coatings based on dichalcogenides of transition metals from Groups IV–VI of the periodic table, inparticular, molybdenum and tungsten disulfides and diselenides ($MoS_2$, $MoSe_2$, $WS_2$, and $WSe_2$), were deposited via the HF cathode sputtering technique described in [1–6]. In disk-on-sphere friction tests, the specific load and the constant sliding rate were ~105 N/cm2 and 0.019 m/s, respectively [1-6]. The coatings were formed on polished samples fabricated from compact $Al_2O_3$ ceramics and SH-15 and 12H18N10T steels. The crystalline structure of the coatings was investigated by means of reflection electron diffraction using an EMR-102 electronograph, and the surface morphology was examined using JXA-841 and JSM-35C electron microscopes. The elemental composition of the prepared coatings was analyzed via characteristic X-ray spectroscopy( a JEM-100C instrument equipped with a CEVEX attachment) and X-ray photoemission spectroscopy (an ESCALAB-5 device).

## III. Experimental Results

To protect work surfaces from wear of friction pairs technology for production of wear-resistant antifriction coatings of variable thickness with high tribological properties [2], is an effective means of protecting the parts, especially made of corrosion-resistant austenitic steels or titanium alloys from wear. Used in modern engineering austenitic stainless steels and titanium alloys have a number of advantages, but these materials are due to the peculiarities of physical and mechanical properties tend to grasp, followed by catastrophic wear, especially under high vacuum. From the coating process parameters to be considered the most important temperature substrate further bias potential applied to the charge of the sample holder, as well as alloying of the applied coating by applying to the working chamber of reactive gas (or gas mixture) and a complex manufacturing replaceable target structure.

Studies have found that when the temperature of the substrate were formed quasi-amorphous, polycrystalline or textured coatings. Crystallite orientation axis textures [10$\bar{1}$0], perpendicular to the substrate surface was observed for $MoS_2$, $MoSe_2$, $WS_2$, $WSe_2$ in the temperature range 473-973K, and the axis [11$\bar{2}$0] - to $MoS_2$ at T = 673-773K [1-4] . Texture growth with the axis [10$\bar{1}$0] formed in all dichalcogenides, whereas the texture with the [11$\bar{2}$0] was detected in the coatings of molybdenum disulfide in the temperature range 673-773K.

*Dependence of the structure from the location of the samples on the plate of holder of substrates.* Research was conducted at the location of coating growth patterns in different places (in the center and the periphery) of the plate of substrate holder. It was found that the location of the sample in the center of the plate oa holder crystallites grow with a preferred orientation in the form of texture with the axes $[10\bar{1}0]$ and $[11\bar{2}0]$, with appropriate substrate temperatures (Fig.1). The axis [0001] was completely disoriented in a plane parallel to the substrate surface. At a distance from the center to the periphery of the board was observed smooth tilting axes $[10\bar{1}0]$ and $[11\bar{2}0]$ direction crystallite orientation with simultaneous central axis [0001] at the center of the radius of the sample holder, wherein the angle of inclination of the axes reached up to $30^0$. Coincidence direction of the electron beam in the column c electronograph radius vector of the center of the plate leads to a symmetric diffraction pattern, and when the sample is moved parallel to the beam view of the diffraction pattern remains unchanged.

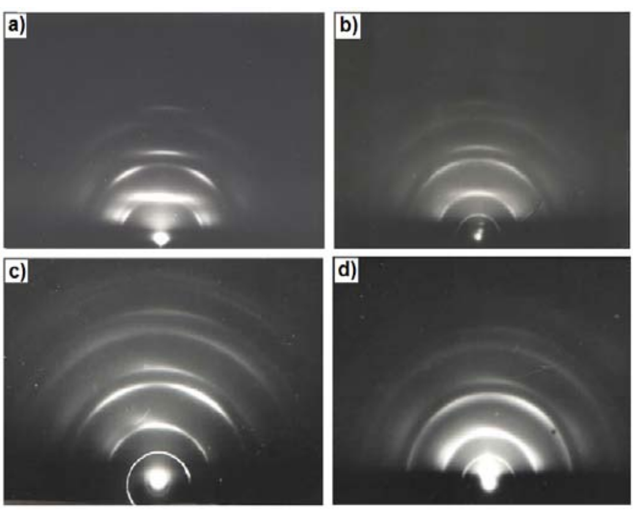


*Figure 1 :* The electron diffraction patterns of coatings $MoS_2$ (a, c) and $WSe_2$ (b, d) a thickness of 0.5 microns, applied at a temperature 523 K ($MoS_2$) and 623 K ($WSe_2$), and the location of samples in the center of the plate (a, b) and at its periphery (c, d)

The results obtained are confirmed by studies of surface morphology of the coating (Fig. 2). Micrograph shows that the crystallites are oriented with a small angular spread. With increasing distance from the center of the board, they form closed concentric circles. This morphology of the films stored at different coating dichalcogenides ($MoSe_2$, $WS_2$, $WSe_2$) (Fig.1,2). Range of crystallization under the same deposition conditions (substrate temperature varied only) shifted into a zone of higher temperatures. The highest transition temperature of the amorphous structure to a crystalline textured observed for tungsten diselenide $WSe_2$ (Fig. 3). Studies shows, that the texture with the axes $[10\bar{1}0]$ and $[11\bar{2}0]$ in the coatings on the basis of textures are dichalcogenides growth, since they do not occur in its infancy, and in the later stages. For example, if a molybdenum disulfide coating on polished samples of steel or $Al_2O_3$ at a temperature of 523K is different along coating thickness.

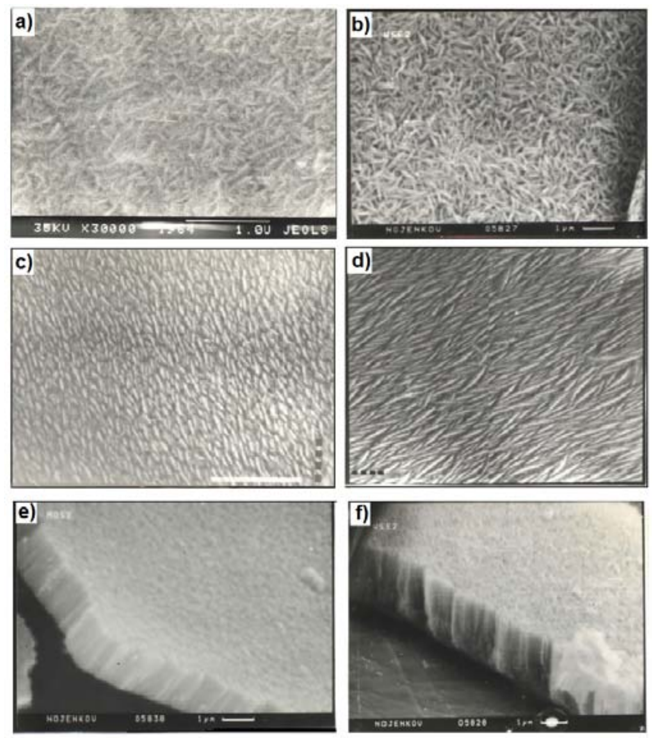


*Figure 2 :* Microgfotoraphs of the surface of (a-d) and cleavages (e, f) coating $MoS_2$ (a, c, e) and $WSe_2$ (b, d, f), applied at a temperature of 523 K ($MoS_2$) to 653 K ($WSe_2$) at location samples in the center of the plate (a, b, e, f) and on its periphery (c, d)

Coating thickness of less than 0.08 m have an amorphous structure and have a smooth surface. When such friction tests showed no anti-friction coating acts as in the case of coating deposition at low substrate temperatures . A similar mechanism of crystallite growth was observed in the coating of aluminum nitride AlN (having a hexagonal crystal structure with a lattice Wurtzite) by magnetron sputtering. As the distance from the center axis of the formed coating $[10\bar{1}0]$ in the presence of simultaneous orientation of the second axis texture [0001] along the radii from the center of the plate (Fig. 4) . As follows from the diffraction pattern, the second axis [0001] at an angle of crystallites to a surface of the substrate up to $15^0$ and the principal axis is tilted textures $[10\bar{1}0]$, respectively, towards the center. When applying vacuum ion-plasma methods and by electron-beam evaporation (REP) coatings of pure molybdenum and chromium and their compounds such as nitrides and oxides with body-centered cubic lattice, in the center of the plate to form a coating samples with texture axis [110]. As the distance to the periphery was a gradual slope texture axis [110] to the center (up to the transition to the texture of a [111] axis) while being oriented to the [100] direction along radii from the center of the plate. I.e. also in this case maintained a similar growth mechanism.

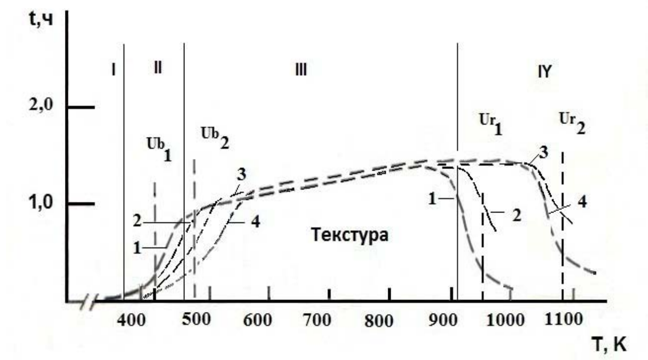


*Figure 3 :* Dependence durability of coatings based on samples of dichalcogenides $Al_2O_3$ substrate temperature Scheme disc-sphere. 1-$MoS_2$; 2-$MoSe_2$; 3 - $WS_2$; 4 - $WSe_2$; I - The amorphous structure; II - Polycrystal; III - Texture; IY - Area expansion dichalcogenide $MX_2$ on metal and halcogen; $Ub_{1,2}$ - surface potential barrier and $MoS_2$ and $WSe_2$ ; $Ur_{1,2}$ - energy decomposition dichalcogenides $MoS_2$ and $WSe_2$

Microphotographs (Fig.4) is not visible almost two-dimensional elongation of the crystals, as in the case of transition-metal dichalcogenides, due to the lack of such a large anisotropy of the surface energy of crystal faces. $Cr_2O_3$ coating had a hexagonal structure, space group $D^6_{3d}$-3RS. Crystal growth $Cr_2O_3$ obey the same law - in the center of the plate texture is formed with the axis $[10\bar{1}0]$ perpendicular to the substrate surface.

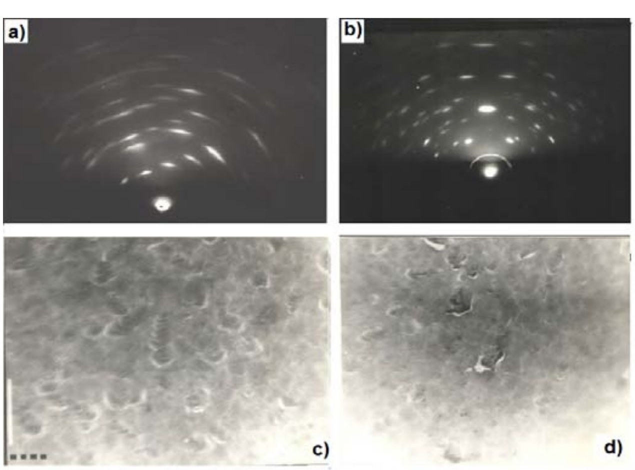


*Figure 4 :* Electron diffraction (a, b) and micrographs (x5000) (c, d) coating AlN (a) and $Cr_2O_3$ (b, c, d)

When removing the periphery occurs smoothly tilt axes $[10\bar{1}0]$ towards the center with simultaneous orientation [0001] axis along the radii from the center of the sample holder. As the distance from the center of the coating formed with the $[10\bar{1}0]$ in the presence of simultaneous orientation of the second axis texture [0001] along the radii from the center of the plate (Fig. 4). As follows from the diffraction pattern, the second axis [0001] at an angle of crystallites to a surface of the substrate up to $15^0$ and the principal axis is tilted texture $[10\bar{1}0]$ toward the center respectively. Improving tribological properties of the coatings is possible with the changes in technology application. For example, increasing the hardness of the substrate reduces the coefficient of friction and increased durability of coatings based dichalcogenides. Improved tribological characteristics occurs when doping atoms of molybdenum disulfide additional element. The combination of applying a wear-resistant outer sublayer with doping atoms antifriction layers additional element can significantly improve the tribological characteristics.

*Doped coating.* Were obtained from the doped molybdenum disulfide coating composition MoS2Dx that appearance is not much different from conventional coatings MoS2. As dopant D can be selected elements or compounds that do not form strong (chemical) bonds with the host lattice $MoS_2$. When friction testing scheme disk sphere coatings with a hexagonal crystal structure of molybdenum disulfide 2H-$MoS_2$ were obtained sufficiently low coefficient of friction, but in general the corresponding friction natural molybdenum disulfide. However, friction tests in the same conditions coating composition $MoS_2D_x$ led to getting unusually low values of the coefficient of friction (effect of superlow friction) (Fig.5).

Electron diffraction studies of coatings $MoS_2D_x$ showed that there was a significant increase them ¬ crease the lattice period along the axis c (up to 1.38-1.43 nm against 1.2295 nm for compounds with a stoichiometric composition (hexagonal 2H-$MoS_2$) in practically constant period along the a axis . Increasing the distance between the layers when placing the D atoms in the inter-packet spaces due to the fact that the energy of the van der Waals interaction varies in proportion to $\sim r^{-6}$, should lead to a decrease in this interaction practically an order of magnitude [1-6].

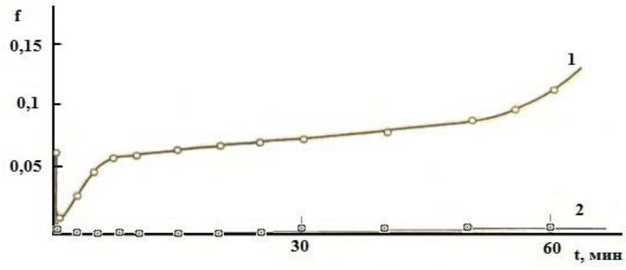


*Figure 5 :* Coefficient of friction on the duration of the test coatings doped $MoS_2$ (*1* - $MoS_2$; *2* - $MoS_2D_x$)

Anti-friction coating with wear resistant underlayer. In magnetron sputtering a target of pure molybdenum in an atmosphere of nitrogen was obtained from the compound coating type molybdenum nitride (solid solution) with high microhardness (Vickers hardness scale (HV) 1,400 kgf/mm$^2$). Molybdenum nitride forms cubic crystals with lattice period a = 0,4163 nm. With the application of the technology [1-6] have been applied to the coating composition variable along thickness of the wear layer composition to the antifriction ($M_kN$ - $M_kN_mX_n$ - $MX_2D_X$), in which the outer sliding layer of $MoS_2$ stoichiometric composition was replaced with an additional layer $MX_2D_X$ alloying element D. Coating $MoS_2D_X$ led to ultralow values of the coefficient of friction on the air under normal conditions (Fig.5,6).

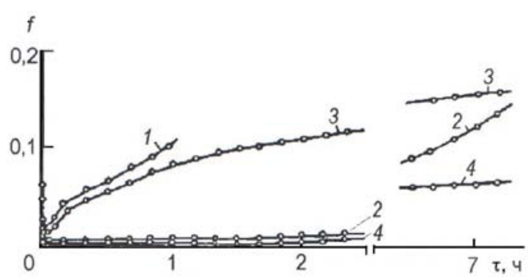


*Figure 6 :* Dependence of the friction coefficient on the duration of the test coatings: 1 - $MoS_2$; 2 - $MoS_2Д_x$,; 3 - ($Mo_2N$- $M_kN_mX_n$ - $MoS_2$); 4 - ($Mo_2N$- $M_kN_mX_n$- $MoS_2Д_x$)

Studies were carried out properties of the composite anti-friction wear-resistant coating based on tungsten diselenide and disulfide WS2 and WSe2, deposited on a substrate made of structural strength titanium alloy VT23, and gallium alloyed coating WS2Gax and WSe2Gax (Fig. 7), deposited on a substrate by reactive electron-beam plasma spraying (RAP) as wear $Cr_2O_3$ sublayer thickness of 2.0-2.5 microns.

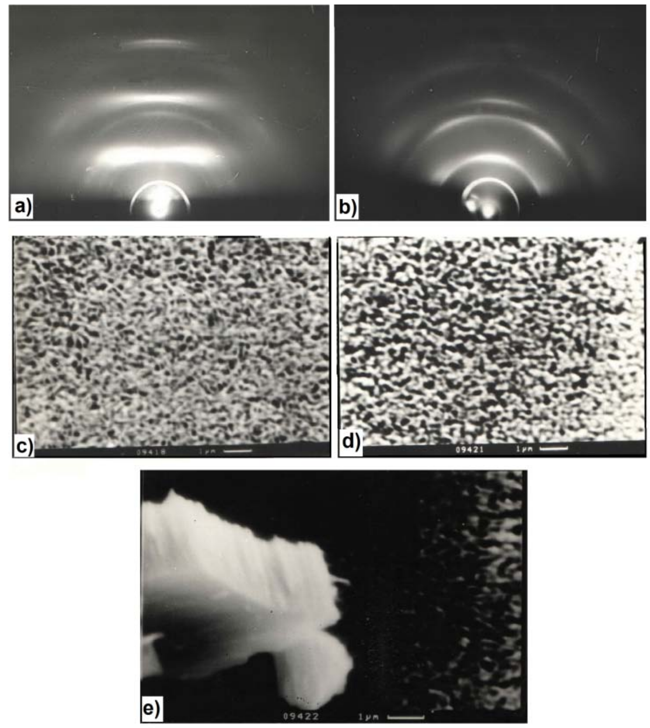


*Figure 7 :* Electron diffraction (a, b) and micrographs (x5000) (c, d, e) coating $WS_2Ga_x$

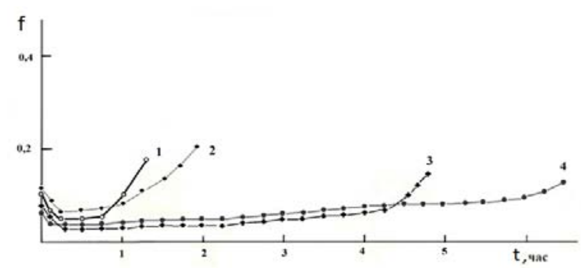


*Figure 8 :* Dependence of the friction coefficient on the duration of the test doped coatings $WS_2$ and $WSe_2$ with wear sublayer $Cr_2O_3$, deposited on titanium alloys: (*1* - $WS_2$; *2* - $WSe_2$; *3* - $WSe_2Ga_x$; *4* - $WS_2Ga_x$)

Coatings based on dichalcogenides $WS_2$ and $WSe_2$ had a hexagonal structure, crystal growth corresponded to the above atomic cluster model of crystallization on the formation of smooth periphery texture with two axes type mosaic crystal. Doping gallium of $WS_2$ and $WSe_2$ coatings led to a significant increase in their tribo-technical properties (Fig. 8).

## IV. Disscussion of Results

Based on the concepts of migration processes of atoms on the surfaces of solids, along with a rough structure of atomically smooth areas, created a generalized mathematical model of the application and obtained the properties of ion-plasma coatings, determining their structure during application and physico-mechanical properties of the coatings when applying such coatings[1-6].

On the basis of established generalized theoretical model:

- Application developed atomic cluster model of crystal growth in the coating vapor deposition or the flow of sputtered particles in vacuum, caused by the presence of two phases on the surface of the atoms (condensed and migratory) and phase transitions occurring in a temperature range on the substrate;
- Proposed and experimentally substantiated mechanism of action of anti-friction coatings doped dichalcogenides explaining the effect of superlow friction solid laminates and defining opportunities for ultralow friction. The essence of atomic cluster model of crystal growth is as follows: Atoms in the adsorption sites in the "sedentary state" on a solid surface are condensed phase. Migratory phase can be represented as two-dimensional gas on the surface that follows an exponential distribution of particle energies (Maxwell distribution). The ratio of the two phases determines the structural state of the growing coating. Then the crystal size L in a growing number of the coating is determined by the ratio of the condensed phase (defined by B) and the migratory phase (defined by C).

$$L = A\,[(1-\varepsilon)B + \varepsilon C]^{1\backslash 2} \qquad /\ 1\ /$$

where A - value depending on the structure and properties of deposited material.

Flux of sputtered material in vacuum ion-plasma deposition methods, along with the atomic phase contains a certain number of cluster phase consisting of N atoms (for N = 1,2,3 and more). Such polarized clusters in the coating on the surface can be oriented properly and around the center of the board and play a role in the crystallization step coverage, identifying the growing structure. Decisive influence should provide flow distribution of the deposited particles on the cosine law. Thus facets with the highest surface energy should rise with a slope in the direction of maximum density of flux, which particles with the cosinusoidal distribution of the target is in the center. Under the influence of these factors together formed texture with two axes preferred orientation of crystallites, with properties approaching the single crystal (Fig.1, 2).

With increasing temperature observed broadening of the distribution curve of the particle energy, the displacement magnitude of the potential barrier at higher temperatures should be an increase in the width of the crystallization. As indicated above, this occurs, for example, in the case of transition metal dichalcogenides, wherein the smallest width of the crystallization for $MoS_2$ (373 ... 413 K, and, most - for $WSe_2$ (493 ... 563 K). Therefore, when the displacement magnitude of potential barrier to absolute zero can be achieved practically hopping phase transition type crystallization (Fig. 9), which may occurs, for example, in the time of the transition from the normal state to the superconducting.

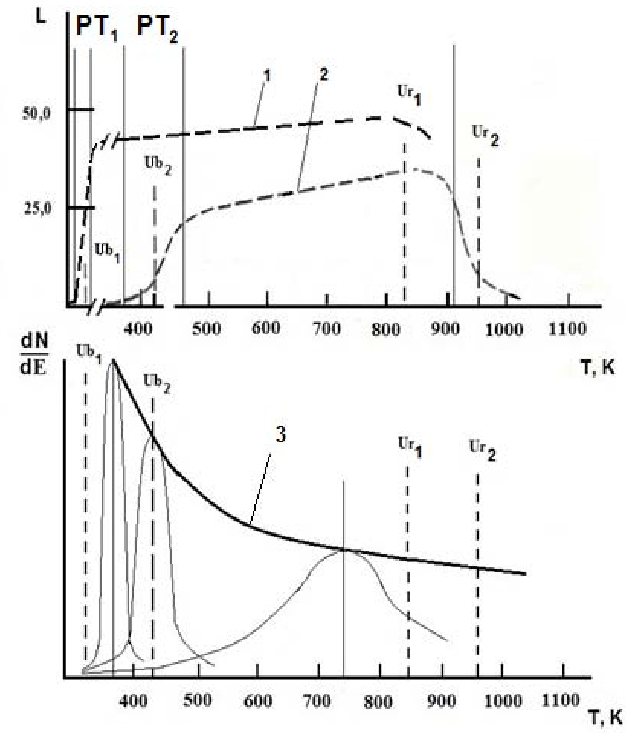


*Figure 9 :* Dependence characteristics L (a) and the particle energy distribution (b) of temperature

Curve 1, 2 - L value specifications for compounds $MX_2$ (1 or 2);

Curve 3 - envelope of the inflection points of the energy distribution of particles $MX_2$ (1 or 2);

$Ub_{1,2}$ - $MX_2$ surface potential barrier (1 or 2 );

$Ur_{1,2}$ - $MX_2$ binding energy (1 or 2 );

$PT_1$ and $PT_2$ - phase transitions.

*Antifriction mechanism of action,* explaining the occurrence of the effect of superlow friction solid laminates based dichalcogenides and defining high tribological properties of the coatings during friction, cracking easily justified crystals on planes (0001) dichalcogenide packages where there are weak van der Waals interactions of the type, not related to the exchange or socialization electrons, and allow ease of sliding such packets to each other. Terms of superlow friction coefficients are presented in [1-6]. Determining factor in this process is to not break the binding energies of Ur in the contact zone, and the shift of the atomic planes overcoming potential barriers sliding over each other surfaces Ub. In the study of changes in the surface layers during friction dichalcogenides found that the structure of crystals with preferred orientation (texture ) with the axis $[10\bar{1}0]$ turns into a texture with the [0001] direction perpendicular to the substrate.

The emergence of superlow friction due to the presence of migratory phase on friction surfaces (0001), in a state of two-dimensional gas. In [1-6] the occurrence of this phenomenon is determined by the coefficient of slip $K_s$ ratio of condensed $B_s$ and migratory $C_s$ phases through the dependence

$$K_s = A_a [(1- \varepsilon)B_s + \varepsilon C_s]^{1\backslash 2} \qquad / \ 2 \ /$$

where $A_a$ - value depending on the structure and properties of applied substance.

The particles of this phase (atoms , molecules, clusters) can be adsorbed from the environment or introduced into the lattice of solid as it is formed . For superlow friction coefficients in normal air must shift the phase transition in the temperature range of less than 300 K , i.e. the binding energy of atoms adsorbed on the (0001) plane dihalcogenide to ensure free movement on the surface to be less than the kinetic energy of the atom under normal conditions. Mass transfer without heat loss and energy costs possible along the equipotential surface. Having alloy monolayers of particles on the surfaces of friction increases the distance between the planes (0001) and reduces the interaction energy between the layers $U_r$. Such particles when opportunities for migration of the diffusion surface (0001) provide ease of sliding the opposed planes (0001) relative to each other and thus by moving the particles along the field lines of the surface ( 0001 ) arises the possibility of movement without energy dissipation.

In the absence of a condensed phase is preserved only migratory phase

$$K_s = A_a (\varepsilon C_s)^{1\backslash 2} \qquad / \ 3 \ /,$$

provides the effect of superlow friction.

## V. Superlow Interaction between Particles

Discovered physical phenomenon of mass transport along the lines of equipotential surface fields without energy dissipation in the absence of resistance forces is a process of moving the motion of matter, manifested in the form of ultra-low friction, superconductivity and superfluidity. This movement is possible under normal conditions in the form of particles moving between the solid surface along the lines of equipotential fields determined the shape and structure of the Fermi surface.

An unusual feature of the motion of particles (atoms, molecules, clusters) of homogeneous singular planes (0001) dichalcogenides is uniform motion without energy dissipation. Similar phenomena have been observed to create the conditions for the movement of particles in the absence of frictional forces (superfluidity) and resistance to movement of particles (superconductivity). Intercalation dichalcogenides which are semiconductors, led to the emergence of their superconducting properties, which was a consequence of placement of dopant atoms in the interlayer spaces. Superlow friction phenomena and superconductivity observed in layered crystal structures of type dichalcogenides ($MX_2$) and diboride ($MB_2$) metals [1-6]. In magnesium diboride $MgB_2$ was discovered high-temperature superconductivity for a simple chemical compound critical temperature of 39 K, due to the presence in $MgB_2$ energy gap is not one but two . In the superconducting magnesium diboride present two kinds of Cooper pairs. Their interaction provides a sufficiently high temperature Superconductivity. It is important to note that each class has its electron pairs size, or its coherence length. Wherein magnesium diboride is only one value of the London penetration depth.

In [5,6] studied the movement of negatively charged electron around the positive proton in the hydrogen system with the absence of dissipation in the uniform motion. To preserve the symmetry of Riemann and Lobachevsky fields opposite curvature in such systems, there exists the possibility of geometrical rectilinear motion of a particle in the absence of centripetal forces, the conservation movement at a constant speed . In this case, there is no change in the energy of the moving particles, i.e. the absence of dissipation. Anisotropic properties dihalcogenides and diboride preserves mass transfer phenomena dissipationless along equipotential surfaces fields determined the shape and structure of the Fermi surface at a sufficiently high temperature. Placement of dopant particles in the interlayer spaces along the plane ( 0001 ) causes the mass to move at a constant speed without dissipation of energy, i.e. there is the possibility of zero change of the interaction energy with the solid surface during the movement (a phenomenon superlow friction).

High-temperature transport mass without dissipation is possible along the lines of equipotential surfaces (0001) layered anisotropic compounds in the presence of a layered structure of the solid body spaces van der Waals forces. Owing to the special status of the layered solid body - the availability of space Van der Waals forces - which are long-range forces of the dispersion and no free valence electrons capable of forming strong exchange interactions, there is the possibility of moving particles without dissipation (scattering) energy.

Interaction between packages of dichalcogenide X-M-X (X – chalcogen; M - metal) have dispersion nature, which are based on the dipoles formed by the action of collective phonon vibrations of the atoms inside the package X -M - X . These vibrations cause additive phonon vibrations associated with the polarization of opposite sign in the nearby package. Additivity of the dispersion interaction (unlike pair interactions of exchange type) causes its long-range nature of this interaction and potential decreases with increasing size of the gap by doping dichalcogenide by law $r^{-2}$ , up to n = 2.

Dissipative processes are the result of the forces of resistance arising from the exchange interaction processes.

## VI. Conclusions

- Drawing doped multilayer coatings enables obtaining ultralow friction under normal environmental conditions and increases the durability of the coating several times.
- The phenomenon of non-dissipative mass transfer along the equipotential surfaces of fields that define the shape and structure of the Fermi surface.
- Established that ultra low friction, superconductivity and superfluidity are related phenomena defined phase transition through the critical value of the characteristic parameter (energy potential barrier) Fermi surfaces. Creation of the composite coatings of variable thickness of the wear layer doped to antifriction of high anti-friction and wear-resistant properties.

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