Thickness of vibrational mechanochemical solid-lubricant coating in friction pairs of transport engineering products

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Abstract. The paper studies the thickness of the vibrational mechanochemical solid-lubricant coating of molybdenum disulfide which is widely used in transport and technological systems.

1. Introduction
The unique properties of solid-lubricant coatings based on molybdenum disulfide (MoS₂) and no less unique features of vibrational mechanochemistry are the basis for increasing wear resistance of the responsible parts in friction of various products of the transport complex [1-13]. The purpose of this study was to determine the processing time of the thickness of solid-lubricant coating based on molybdenum disulfide (MoS₂) and to compare it with the coating applied manually.

2. Theoretical part
One of the main impacts which determines the formation of vibrational mechanochemical coatings is a chemical process that can take place if the energy threshold at which the reaction is feasible has been overcome. Further, a metered energy supply is required. Controllability of this process most fully ensures the mechanical impact of free-moving indenters.

In general, the energy model of vibrational mechanic chemical coatings formation can be presented in the form of:

\[ U_a > U_{mg} \pm U_{xg}, \]

where \( U_a \) is energy required to conduct the chemical reaction; \( U_{mg} \) – external mechanical energy; \( U_{xg} \) - additional energy used to accelerate the chemical reaction (sign “+”) or spent (sign “-”) to compensate losses during the chemical reaction.

The boundary condition of the model can be a criterion:

\[ U_{mg} \leq U_{mmax} \]

where \( U_{mmax} \) – limits of the energy capabilities of the mechanical component of the process.

Analysis of the criteria (1) and (2) shows that it is necessary to determine variants of the chemical effects with the highest rate of the internal energy which ensures an intensive chemical reaction to achieve the required technological -indicator. Then the external mechanical energy can be provided by its adjusted supply into the processing area, for example by the wave process. In this case, the energy loss(minus \( U_{xg} \)) in formula (1) can be reduced, which will increase the share of energy (\( U_{mg} \)) to intensify
the chemical reactions and give significant energy saving of the coating formation process.

In accordance with the basic law of thermodynamics - the law of energy conservation, under its transformations, the equation of the energy balance in the chemical-mechanical process of the local micro volume coating formation on the border of the section "coating-substrate" can be written:

$$\Delta U = \Delta U_{pm} + \Delta U_{pc} + \Delta U_{tm} + \Delta U_{tc},$$  (3)

where \( \Delta U_{pm}, \Delta U_{pc} \) - change in the mechanical and chemical potential component of the internal energy of the local volume; \( \Delta U_{tm}, \Delta U_{tc} \) - part of the thermal energy spent to increase its energy condition.

The ratios between the components of the energy balance of the chemical-mechanical process in the formation of vibrational mechanic chemical coatings can be very diverse and depend on the nature and material structure, as well as the conditions in which the coating process takes place. Considering the modified local microvolume formed in the process of vibrational mechanic chemical processing at the border of the section “coating-substrate” as an open thermodynamic system in the certain chemical-mechanical conditions, in the local equilibrium, the condition for its formation can be presented in the form of:

$$\Delta U = U_0$$  (4)

where, \( \Delta U, U_0 \) - respectively, change in the molar internal energy system and its molar energy, which determines the conditions for the formation of modified local micro volume.

With consideration of the Gibbs’ excess method, Boltzmann's interpretation of entropy, and the free energy change in the local micro volume during the chemical interaction of the coating components, was obtained a model that reveals the mechanism of chemical-mechanical synthesis of coating formation in the conditions of vibrating technological systems that determine the energy state of local microvolumes on the border of the "coating-substrate" section modified during the vibrational mechanic chemical processing:

$$U_0 = TR\ln\left(\frac{\tau}{\tau_0}\right) + 10^{-6}V_m\left(\frac{\sigma_e^2}{2E} + K_\sigma \sigma_e \frac{d}{D}\right) - \Delta G^\circ,$$  (5)

where - \( \tau \) - time when the system is under the chemical and mechanical impact; \( \tau_0 \) - period of thermal oscillations of atoms \( 10^{-12} \) c; \( V_m \) - molar volume, mm\(^3\)/mole; - \( \sigma_e \) - effective voltage, MPa; \( E \) - elasticity module, MPa; \( d \) - diameter of the plastic print that is formed on the surface under the hit of the working area indenters with the diameter \( \phi D \); \( K_\sigma \) – the heat coefficient; \( \Delta G^\circ \) - change of free energy Gibbs, KJ/mole.

The energy model takes into account the contribution of bound energy to the formation process of vibrational mechanochemical coatings of the surface layer due to the growth of entropy (first term), energy increase of elastoplastic distortions of the crystal lattice as a result of mechanical effect of indenters (second term), changes in the internal energy of the surface layer, modified as a result of chemical interaction of the contacting materials (third term). The role of each of them in the cynetics of forming classification groups of mechanochemical coatings is described by energy and type models, which show that the main contribution to the process of formation of vibrational mechanochemical coatings of the first group is made by the deformation term which monotonously grows over the time.

The formation of vibrational mechanicchemical coatings of the second group is the result of deformation and chemical terms. When vibrational mechanochemical coatings of the third group are formed, the leading role belongs to the chemical component of the model.

The main indicator of the quality of the coating applied to the surface of the metal is adhesion, which characterizes strength of adhesion between two materials, emergence of the connection between the surface layers of two different substances, brought to the contact. If we equate the molar energy determining the formation conditions of the modified local microvolume on the border "coating-substrate" to the average energy of binding unit providing its adhesion, then on the energy model basis we can receive calculation-analytical model of the technological system, which provides the coating on the material surface required by the operating conditions of the products:
\[ E_a = T R \ln \left( \frac{1}{\tau_0} \right) + 10^{-6} V_m \left( \frac{\sigma^2}{2 E} + K_A \sigma \varepsilon \frac{d}{D} \right) - \Delta G^* . \]  

The calculation analytical model of the coating application technology system allows at the stage of technological production solving a number of optimization tasks with the aim to design technological processes, which ensure the required quality and performance features of the surface parts.

On the basis of the calculation-analytical model, a generalized formula was received to estimate the duration of the process of vibrational mechanic chemical processing. The process of formation of the vibrational chemical mechanical coating finishes at the time \( \tau = \tau_p \), when plastic deformation of the surface in the process of dispatch impulsive impact of free-moving indenters reaches the limit for this material, i.e. \( d = d_{\text{pr}} \), and activity of the system components reaches the thermodynamic constant of equilibrium.

By extraction of \( \tau_p \), we will get the generalized formula for process duration estimation of the formation of vibrational mechanic chemical coatings:

\[ \tau_p = \tau_0 \exp \left[ \frac{E_a - 10^{-6} V_m \left( \frac{\sigma^2}{2 E} + K_A \sigma \varepsilon \frac{d}{D} \right)}{RT} - \Delta G^* \right]. \]  

3. Materials and methods

The effect of processing time on the thickness of the coating was studied on the coating obtained with vibrational processing amplitude 2.5-3 mm and the vibration frequency of the working chamber - 33.3 Hz. Processing time - 180 minutes. Determination of the thickness of the coating by weighing in the first 30 minutes was done in 10 minutes after the processing, then the interval was 30 minutes. Dependence of thickness and morphology of the coating from the processing time is shown on (Figure 1).

![Figure 1. Dependence of the thickness of MoS₂ coating on the processing time: 1 - annealed, 2 - hardened; b-morphology of vibration coating.](image)

As you can see from the figure, there is an increase in the thickness of the coating within 30 minutes. Then it stabilizes and remains almost constant during further processing. This is clear from the inspection results of the thickness of the coating [3-6] using the “Colomax” device. The functioning principle of this device is that the rotating ball rubs through the coating to the base metal. The operation scheme is shown on Figure 2.
4. Results

As a result of the round indenter installation with the diameter of 20 mm, two diameters were formed into the surface of the coating: the maximum showing the boundary and the minimum defining the boundary of the metal [3]. Calculation of the difference between the two diameters resulted in a numerical value of the thickness of the coating (Figure 3. a) equal to 3.54 microns, (Figure 3. b) equal to 4.73 microns, (Figure 3. c) equal to 5.81 microns for 30, 60 and 90 minutes, respectively.

The studies of the sample coated with a brush showed that its thickness is half less than that formed in the conditions of the vibrating wave impact and is 2.41 microns. (Figure 4).

Figure 2. Operation scheme of the “Colomax” device.

Figure 3. The thickness of hard-lubricant coating of molybdenum disulfide scale 100mcm; a- 30 min. processing; b- 60 min. processing; c -90 min processing.

For comparison, the picture of the molybdenum disulfide coating applied by a brush is presented. This method is widely used in engineering and aircraft manufacturing plants for the parts of friction pairs.
The drawbacks of this method are evident when analyzing the image of the surface covered with the disulfide molybdenum:
- above the surface of the coating tower plates of molybdenum disulfide, hence the efforts of the brush are not enough to form a compacted uniform coating;
- molybdenum disulfide is not crushed and therefore its implantation into the micro/nano profile of the metal surface is impossible. In this regard, the adhesion ability of the coating is disturbed and as a result its life time.

However, determination of the processing time, in terms of the effect on the thickness of the coating, is not enough. It is necessary to obtain the coating not only with the greatest thickness but with good strength of adhesion and coating integrity. With this purpose, studies of the density and integrity of the coating by microscopic method were performed. Samples –of thin sections were covered by MoS$_2$ for 30, 60 and 90 minutes. Then the surface perpendicular to the processed surface was photographed onto a metallographic microscope MIM – 8 M. MoS$_2$ film, which was applied on the 45 steel sample surface throughout 30 minutes is shown as an example. These microphotographs clearly show that 30 minutes of processing is not enough to form a solid layer of lubricant. This was proved during the production tests when MoS$_2$ was applied (Figure 5).

![Figure 5](image_url)

**Figure 5.** Microphotography of the MoS$_2$ film on the sample of steel 45, after 30 minutes of processing, x 2000.

The studies of the micro-hardness of the hard lubricant coating were conducted on pre-polished steel samples 45, the size of all the samples was 10 x 10 mm. The micro-hardness of the original surface is shown on (Figure 6).

![Figure 6](image_url)

**Figure 6.** a-Original Steel Sample 45. platform 500-1000 nm- b - max 0.21(GPa). T=30 min; c -max 0.31(GPa). T=60 min.

The micro-hardness of the original steel sample 45 was max 3.67(GPa). After the coating application the estimation was done in the same zone, but this time the molybdenum disulfide hardness was determined.
5. Conclusions
The results show that hardness of the molybdenum disulfide coating increases during the processing. However, the wide spread of data should be noted. This is due to the fact that the indenter shows the information of one or several particles of molybdenum disulfide. Therefore, the micro-hardness of the vibrational mechanochemical solid-lubricant coating of molybdenum disulfide is less than that of the main metal. As a result of the performed studies, the time, formation of the coating, its thickness, the difference in the morphology of the coating surfaces were determined. The surface hardness was determined.

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