Chemical and mechanical bases of coating application in vibration technological systems

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Abstract. The article presents the study of vibrational chemico-mechanical coatings. The energy model of coating formation in vibration technological systems is proposed. The classification is developed depending on the energy capacity of the system (the nature and intensity of the processes occurring between the base and the coating). The advantages of vibrational chemical-mechanical coatings over traditional coating and the scope of their practical application are shown. Comparative trials of vibrational chemico-mechanical coatings (Vamp) formed using this vibratory equipment and coatings obtained by conventional methods (electroplating, manual application have demonstrated a number of undeniable advantages and quality indicators of vibrational chemico-mechanical coatings.

1. Introduction
Vibration chemical and mechanical coatings are the result of a combined synthesis of various types of energy effects on the metal surface. The distinctive feature of vibration chemical and mechanical coatings from other coating methods is that its formation occurs under the mechanical vibration impact of the indenter (working environment). As a result of dynamic action, the activation of chemical and physicochemical processes occurring in the surface layer is ensured, and its geometric and physical and mechanical characteristics change [1-12]. Interest in these coatings is associated with the creation of new types of products, the emergence of new requirements for surface quality and is due to a number of advantages over traditional coating methods such as: simultaneous mechanical surface treatment, good appearance of the coating; increased corrosion resistance; increased wear resistance; simplicity of equipment design due to the absence of current leads; hydrogenation of the surface layer of the coating; coverings possible for «hard covering» metals; possible coprecipitation of various metals; using a small amount of chemicals in the solution; less stringent requirements for preliminary surface preparation. For design and practical implementation of vibration chemical and mechanical coatings by controlling the technological parameters of mechanical vibration wave action a set of studies was carried out aimed at developing model representations of the mechanism of formation of vibration coatings and determining their energy state; establishing the patterns of their application, taking into account the specifics and functional purpose [13-20].

2. Methodical part (theoretical aspect)
One of the main influences determining the vibration chemical and mechanical coatings formation is a chemical process, the course of which is possible if the energy threshold is overcome, at which the
reaction is feasible. Further, a metered supply of energy is required. The controllability of this process most fully provides the mechanical action of free-moving indenters [1, 5, 9].

In general, the energy model of vibration chemical and mechanical coatings formation can be represented as:

\[ U_a > U_{sg} \pm U_{sg}, \]  

(1)

where \( U_a \) – energy required for a chemical reaction to occur; \( U_{sg} \) – mechanical energy supplied from outside; \( U_{sg} \) – additional energy supplied to accelerate a chemical reaction (mark \( \pm \)) or spent (mark \( \mp \)) to compensate for losses during a chemical reaction.

The boundary condition of the model can be the criterion:

\[ U_{sg} \leq U_{s\max}, \]  

(2)

where \( U_{s\max} \) – limiting energy capabilities of the mechanical component of the process.

Analysis of criteria (1) and (2) shows that it is required to establish the options for chemical action, in which the internal energy will have the highest rate, providing an intense chemical reaction to achieve the required technological indicator. Then external mechanical energy can be provided by its regulated supply to the treatment zone, for example, by a wave process. In this case, energy losses (minus \( U_{sg} \)) in the formula (1) can be reduced, which will increase the share of energy \( (U_{sg}) \) to the intensification of chemical reactions and will give significant energy saving in the process of forming the coating.

In accordance with the basic law of thermodynamics – law of energy conservation, during its transformations, the energy balance equation for the chemical-mechanical process of the formation of a local microvolume of the coating at the «coating-substrate» interface can be written:

\[ \Delta U = \Delta U_{me} + \Delta U_{ac} + \Delta U_{me}^c + \Delta U_{tc}, \]  

(3)

where, \( \Delta U_{me}, \Delta U_{ac} \) – change in the mechanical and chemical potential components of the internal energy of the local volume; \( \Delta U_{me}^c, \Delta U_{tc} \) – part of heat energy, spent on increasing its energy state.

Relationships between the components of the energy balance of the chemical-mechanical process during the vibration chemical and mechanical coatings formation can be very diverse and depend on the nature and structure of the material, as well as the conditions in which the coating process takes place. Considering the formed in the process vibration chemical and mechanical coatings at the «coating-backing» boundary modified local microvolume as an open thermodynamic system located, under steady chemical and mechanical conditions, in the local equilibrium ratio, the condition for its formation can be represented as:

\[ \Delta U = U_0, \]  

(4)

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

Taking into account the method of excess Gibbs values, interpretation of the entropy by Boltzmann, as well as a change in free energy in a local microvolume in the process of chemical interaction of coating components, a model was obtained that reveals the mechanism of chemical-mechanical synthesis of coatings formation under conditions of vibration-wave technological systems that determine the energy state of local micro volumes at the «coating-backing» boundary modified in the vibration chemical and mechanical coatings process:

\[ U_0 = TRln \left( \frac{\tau}{\tau_0} \right) + 10^{-6}V_m \left( \frac{a^2}{2E} + K_a \sigma_d \right) - \Delta G^o, \]  

(5)

where \( \tau \) – residence time of the system in a state of chemical-mechanical action; \( \tau_0 \) – period of atom thermal vibrations \( 10^{-12} \); \( V_m \) – molar volume, \( \text{mm}^3/\text{mol} \); \( \sigma_d \) – effective stress, \( \text{MPa} \); \( E \) – elastic modulus, \( \text{MPa} \); \( d \) – the diameter of the plastic indentation formed on the surface upon impact of the working medium indenters with a diameter \( \phi D \); \( K_a \) – thermal effect factor; \( \Delta G^o \) – change in Gibbs free energy, \( \text{kJ/mol} \).
The energy model takes into account the contribution of the surface layer of bound energy to the formation of vibration chemical and mechanical coatings due to the growth of entropy (first term), increase in the energy of elastoplastic distortions of the crystal lattice as a result of the mechanical action of indenters (second term), changes in the internal energy of the surface layer modified as a result of chemical interaction of contacting media (third term). The role of each of them in the kinetics of the formation of classification groups of chemical-mechanical coatings is described by the energy and typical models, from which it can be seen that the main contribution to the vibration chemical and mechanical coatings formation of the first group is made by the deformation term, which monotonically increases with time. Formation of vibration chemical and mechanical coatings of the second group – is a result of deformation and chemical terms. When forming vibration chemical and mechanical coatings of the third group, the leading role belongs to the chemical component of the model.

The main indicator of the quality of the coating applied to the metal surface is adhesion, which characterizes the adhesion strength between two materials, the occurrence of a bond between the surface layers of two dissimilar substances brought into contact. If we equate the molar energy, which determines the conditions for the formation of a modified local microvolume at the «coating-backing» boundary, to the average energy of a bond unit that ensures its adhesion, then on the basis of the energy model, a computational and analytical model of the technological system is obtained, which provides a coating on the surface of the material required by the operating conditions of the products:

$$E_a = TR\ln\left(\frac{\tau}{\tau_0}\right) + 10^{-6}V_m\left(\frac{\sigma_d^2}{2E} + K_a\sigma_d^d\right) - \Delta G^\circ.$$  \hspace{1cm} (6)

The computational and analytical model of the technological system for applying coatings allows at the stage of technological preparation of production to solve a number of optimization problems for the design of technological processes that ensure the receipt of the required quality and operational properties of the surface of parts.

Based on the computational and analytical model, a generalized formula was obtained to estimate the duration of the process (vibration chemical and mechanical coatings). At a moment in time $\tau = \tau_n$, when the plastic deformation of the surface that occurs during the shock-impulse action of free-moving indenters becomes limiting for a given material, i.e. $ed = d_{np}$, and the activity of the system components reaches the thermodynamic equilibrium constant, the formation of a vibrational chemical-mechanical coating is completed.

Highlighting $\tau_n$, we get a generalized formula for assessing the duration of the process, the vibration chemical and mechanical coatings formation:

$$\tau_n = \tau_0 e^{\frac{E_a - 10^{-6}V_m\left(\frac{\sigma_d^2}{2E} + K_a\sigma_d^d\right) - \Delta G^\circ}{RT}}.$$  \hspace{1cm} (7)

Analysis of the nature of contacting materials; its physical and chemical properties; features of the formation of each type of coating; the corresponding dynamic loads; the degree of participation of the metal base in the coating formation, allowed vibration chemical and mechanical coatings to classify into 3 groups (Fig. 1). From the classification presented in Figure 1 it follows that some coatings are formed by mechanical approach of the coating material to the metal surface and are held by van der Waals forces, others are formed under chemical reaction conditions, and in the presence of electrostatic forces in the boundary layer, the process becomes more complicated with the formation of an electric double layer, hydration. However, for all vibration chemical and mechanical coatings, regardless of the complexity of chemical processes, mechanical energy invariably remains the main activating force.
3. Results of experimental studies and discussion

The methodological approach to research was based on the principle of a systematic study of the patterns of the formation of vibration chemical and mechanical coatings «up-down» and «down-up». «Up-down» research provided for the miniaturization of traditional microscopic and microelectromechanical studies based on the improvement of methods and processes used by traditional technologies in order to determine the basic requirements for coatings in accordance with state standards; «down-up» research were carried out to study the nanoprofile, structure, morphology of the coating surface, as well as to study the applied material.

The subject of experimental studies of the main classification groups of vibration chemical and mechanical coatings were: structural-phase transformations at the macro and nanoscale, their correlation and influence on the structure and functional properties of the coating, the influence of modes and conditions of coating on the quality characteristics and operational properties of the surface layer. Experimental studies and processing of its results were carried out using modern techniques tested in experimental practice.

Experimental studies were carried out on the UVG 4-10 vibration unit with a chamber volume of 10 liters [9]. Metal, porcelain and glass balls with a diameter of 2-10 mm were used as working media. The studies were carried out under various technological conditions and vibration modes: the vibration amplitude varied from 2 to 5 mm, vibration frequency – 16 to 33 Hz. Coatings were applied to specimens made from the following materials: St3, St20, St40, VT20, AL 9.

Vibration chemical-mechanical solid lubricating coatings based on molybdenum disulfide MoS2. The peculiarity of the formation of coatings of this group lies in the fact that they are applied to the metal surface by particles of the working medium by introducing a finely dispersed dry powder into the surface of the part. Under vibration wave action, particles of the working medium, striking the surface to be treated, bring the applied coating material and the metal surface in the contact zone closer to the occurrence of molecular forces. It was found that the formation of vibration chemical and mechanical coatings of this group largely depends on the intensity of the processes occurring in the zone of direct contact. Under the action of normal and tangential forces, the surface layer of the metal is deformed, with the simultaneous introduction of powder particles.

As a result of repeated shock-impulse action of particles of the working medium, a relatively uniform layer of plastically deformed active metal with a coating is formed on the surface. Thus, an increase in
the internal energy of the surface layers of a metal as a result of plastic deformation leads to an increase in the adsorption activity of metal surfaces, what follows from the vibration chemical and mechanical coatings formation model of the group in question, according to which the initial contact of particles of the working medium, covered by MoS\textsubscript{2}, occurs along the tops of microroughness of the metal surface. In places of contact, areas are formed covered with MoS\textsubscript{2}. During further processing, the powder fills the cavities of microroughnesses, first forming a loose layer, which is subsequently compacted, and a uniform coating is obtained on the surface, the morphology of which is shown at Figure 2.a.

The assess of resulting coating quality shows Figure 2.b, an image of the coating of molybdenum disulfide, applied by the traditional brush method, which is widely used in mechanical engineering and aircraft manufacturing for parts included in friction pairs. Comparative analysis of coatings revealed the disadvantages of the traditional method: the presence of towering plates of molybdenum disulfide above the surface of the coating indicates the insufficient efforts applied by the brush to form a compacted, uniform coating; molybdenum disulfide is not crushed, which does not allow its incorporation into the micro/nano profile of the metal surface and, as a consequence, high adhesive strength of the coating.

![Figure 2](image)

**Figure 2.** a-surface Morphology of vibration chemical and mechanical coatings MoS\textsubscript{2} film, 20 µm scale. b-brush applied scale 10 µm

Vibration chemical and mechanical coatings studies for parts operating under friction conditions of this group have shown that the adsorbed particles of the coating in the contact zone are oriented by reference planes parallel to the treated surface, which can be seen in Figure 3. This orientation of the particles is typical for this group, this predetermines the increased antifriction properties of the surface, and, consequently, an increase in the resource of products in general.

![Figure 3](image)

**Figure 3.** The surface of coated MoS\textsubscript{2} (micro/nanoscale) a-1 µm scale, b – scale 100 nm, v- scaleis 20 nm

The amplitude-frequency characteristics of vibration activation of the process have a significant effect on the formation of coatings. It was found that the maximum growth of the coating is observed at an amplitude of up to 3 mm (Figure 3 9.a). When processing with amplitudes of more than 3 mm the
coating thickness decreases. With an increase in the frequency of vibrations, the thickness of the coating film increases, due to an increase in the number of micro-impacts per unit time. The active growth of the coating occurs, within 30 minutes, then the coating thickness stabilizes and is compacted. With an increase in the processing time over 120 min, the thickness of the coating decreases slightly due to its destruction.

The introduction of this technology made it possible to increase the resource of parts and the reliability of the entire product by 15%, as well as increase the productivity and environmental friendliness of production by 10%.

Of particular interest were the processes occurring at the «metal-coating» boundary, preparation of samples (powder) was carried out according to the following procedure. Vibration chemical-mechanical solid lubricating coatings MoS₂ were applied to specimens of annealed steel (vibration chemical and mechanical coatings). Then, after removing the excess powder from the surface of the samples, the coating was cleaned mechanically, and the surface layer of the metal formed during the treatment was removed. The powder obtained in this way, consisting of MoS₂ particles and a metal of the transition zone, was investigated by different methods.

The obtained data show that the powder mainly contains molybdenum disulfide and support material – α Fe cementite Fe₃C. At the same time, there are lines that indicate the presence of sulfides in the studied powder FeS, FeS₂, and iron oxides FeO, Fe₂O₃, Fe₃O₄.

Under severe friction conditions in air in the contact zone in the presence of sulfur-containing solid lubricants MoS₂ and WS₂ iron oxides and sulfides are formed (FeS, FeS₂). As noted above, chemical interaction occurs under the influence of high pressures or temperatures.

Based on the performed X-ray structural studies, it can be assumed that in this process, due to the high contact pressures exceeding the yield point of the processed material and the temperature in the contact zone, a chemical interaction of the MoS₂ powder occurs at the part surface at the «metal-coating» boundary. A chemically modified boundary layer is formed containing sulfides and partially iron oxides. It has been found that coating MoS₂ leads to a significant decrease in the coefficient of friction with 0.24 in its original state, to 0.19 covered with a brush, and to 0.04 when applying vibration chemical and mechanical coatings, and thus provides a 7-fold increase in the wear resistance of the sample.

4. Conclusions
Scope of use vibration chemical and mechanical coatings in various sectors of the national economy is quite multifaceted and also tends to further expand. Accordingly, the range of further investigations for effective technological application of vibration chemical and mechanical coatings is wide and varied. Research in this area is undoubtedly relevant and promising. They will be able to provide an effective solution to many practical problems.

The versatility and diversified nature of the vibration chemical and mechanical coatings application for solving technological problems is promising in the automotive industry and aviation technology, tractor and agricultural engineering, shipbuilding and the production of household appliances, mining machines and tools, etc. this contributes to an increase in productivity, quality indicators of parts and products and their operational properties, and to solving environmental problems of enterprises.

The energy model made it possible to describe the effect of the coating material and the conditions of the process on the kinetics of changes in the internal energy of local microvolumes, modified during the formation of the coating, obtained as a result of interaction with the metal surface of the working medium under the activating shock-pulse action of granules (metallic or non-metallic).

On the basis of the energy model, a computational and analytical model of a vibrational technological system for coating deposition was obtained, which makes it possible to control the chemical-mechanical synthesis of the process at the stage of technological preparation of production, as well as to solve a number of optimization technological problems to ensure the quality and operational properties of the surface of parts.

The technical and technological problems of vibration chemical and mechanical coatings application were scientifically substantiated and solved on the basis of the developed methodology, algorithm and
program for selecting methods and processing modes that provide the required parameters of the coating quality, taking into account their functional purpose, with a minimum cost. So, for the coatings of the first group, the cost was obtained up to 5 times lower than analogues, for the second group – 2.5 times, for the third – 2.1 times.

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