Thermodynamic aspects of the coating formation through mechanochemical synthesis in vibration technology systems

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Abstract. On the basis of thermodynamic concepts of the process, we proposed an energy model that reflects the mechanochemical essence of coating forming in terms of vibration technology systems, which takes into account the contribution to the formation of the coating, the increase of unavailable energy due to the growth of entropy, the increase in the energy of elastic-plastic crystal lattice distortion as a result of the mechanical influence of working environment indenters, surface layer internal energy change which occurs as a result of chemical interaction of the contacting media. We proposed adhesion strength of the local volume modified through processing as a criterion of the energy condition of the formed coating. We established analytical dependence which helps to obtain the coating strength of the material required by operating conditions.

1. Introduction

The process of forming of mechanochemical coatings is a set of simultaneous chemical and physico-chemical phenomena occurring in the surface layer of metal under the influence of external forces. A distinctive feature of vibration mechanochemical coatings (VMCC), which distinguishes them from other types of coatings, is that their formation occurs under conditions of the vibration shock-pulse impact of indenters, moving freely in the closed volume of the working chamber. As a result of the dynamic interaction of the indenters with the surface of the part, chemical and physicochemical processes occurring in the surface layer are activated and a change in its geometrical and physical and mechanical properties occurs [1, 2].

From the thermodynamic point of view, all elementary acts of the mechanochemical process, taking place in the local micro-volumes at the ‘coating-substrate’ interface, are divided into two distinctive groups, characterized by different kinetic laws [3, 4]. The first group of elementary acts of atomic and molecular rearrangements is associated with the establishment of adhesive bonds between contacting substances and therefore they cause accumulation in the local volume of stored energy. Elementary acts of the second group are connected with establishment and cancellation of connections as a result of the transformation (conversion) of irreversible mechanochemical thermal energy, which results in the form of a thermal effect. Therefore, in accordance with the basic law of thermodynamics - the law of energy conservation during its transformation, the equation of the energy balance of the process of the local micro volume of the vibration mechanochemical coating at the "coating-substrate" interface can be written as follows:
\[ A = \Delta U + q \]  
\[ \Delta U = \Delta U_{pm} + \Delta U_{pch} + \Delta U_{hm} + \Delta U_{hch} \]

where, \( \Delta U_{pm}, \Delta U_{pch} \) – changes in the mechanical and chemical potential component of the local volume of internal energy; \( \Delta U_{hm}, \Delta U_{hch} \) – a part of heat energy expended to increase its energy state; \( q \) – a part of thermal energy dissipated into the substrate body and the environment.

2. The energy model of mechanochemical synthesis of VMCC

Considering mechanochemical processing (VMCP) generated in the course of vibrating at the interface ‘coating-sublayer’, we can present the modified local microvolume as the open thermodynamic system under established mechanochemical conditions in the ratio of local balance. It is possible to present a condition of its formation in the shape of:

\[ \Delta U = U_0, \]  
where \( \Delta U, U_0 \) – change of mole internal energy of the system, and its mole energy, accordingly, defining conditions of formation of the modified local microvolume.

The physical sense of this condition lies in the fact that when the left part, corresponding to an increase of the internal energy of system \( \Delta U \), will reach the right \( U_0 \), estimated by the fundamental power characteristic, the modification process of the local microvolume will reach its completion (balance).

The concept of the surface layer as the phase layer possessing thickness and volume is taken as a basis of thermodynamic approaches to the surface layer description. It allows using the description the same thermodynamic device for the surface layer as that for three-dimensional phases [5]. According to the method of surplus values of Gibbs [6], in compliance with it, the used thermodynamic parameters are not absolute but superfluous in comparison with the corresponding parameters of the macroscopical phases, the fundamental equation for the energy of surface layer energy \( U \) at the interface of the phases separation looks like:

\[ \Delta U = T \Delta S + p \Delta V + \sum \mu_i \Delta \omega_i, \]

where \( T \) – absolute temperature; \( p \) – pressure; \( S, V, \mu_i \) – mole values of entropy, the volume and the chemical potential; \( \Delta \omega_i \) – mole fraction of the i-component of the system.

Consideration of each component under conditions of VMCP has shown that the first summand is a mole excess of connected energy \( \Delta S \) which irreversible growth during any non-equilibrium processes is postulated by the second law of thermodynamics. According to Boltsman’s interpretation, the change of mole entropy is described in the shape of \( \Delta S = R \ln \frac{W_2}{W_1} \).

where \( W_2, W_1 \) - thermodynamic probabilities of the initial and final condition of the system. If we assume that entropy manufacture in the system at VMCP is estimated by the duration of mechanochemical synthesis of the process of coating formation, then the thermodynamic weight of the system can be estimated from the correlation:

\[ \frac{W_2}{W_1} \approx \frac{t}{t_0}, \]

where \( t \) – the time of the system period under the condition of the mechanochemical synthesis; \( t_0 \) – the period of thermal deviation of atoms.

The contribution of mechanical forces to an excess of internal energy of the system is composed of potential energy \( E_{es} \), caused by external and internal (residual) elastic stress, and energy \( \Delta E_{pd} \), accumulated by plastic deformation, which means \( pdV = E_{es} + \Delta E_{pd} \). The change of the mole potential caused by elastic deformations makes:
\[ E_{es} = V_m 10^{-6} \frac{\sigma^2}{2E}, \] (5)

where \( V_m \) – the mole volume, mm\(^3\)/mole; \( \sigma \) – effective stress, MPa; \( E \) – the stress module, MPa.

Elastic energy is not accumulated in a material eventually; therefore, the current value \( E_{es} \) is a function of the instant stresses value. Besides, it is necessary to note that the experimentally established fact proves efficiency of VMCP. In spite of the fact that during elastic deformations, elastic energy is not accumulated in a material eventually, \( E_{es} \) is not equal to zero as microplastic deformations take place.

Unlike \( E_{es} \), the work spent on the plastic deformation, eventually accumulates in a material, and is transferred in this way to the thermodynamic system being at the interface ‘coating – sublayer’. The mechanical energy is equal to mole work of rigid forces, which is equivalent to the square under a true curve ‘stress – deformation’:

\[ \Delta E_{pd} = V_m 10^{-6} \sigma \Delta \varepsilon, \] (6)

where \( \Delta \varepsilon \) - relative change of the plastic deformation of the system under the condition of mechanochemical influence \( t \).

The relative change of the plastic deformation in the course of processing by dynamic methods of surface plastic deformation of free moving indenters (characterized by a small degree of deformation \( \Delta \varepsilon \leq 0.3 \Delta \varepsilon \)), which variety is vibrational-striking processing, can be estimated by correlation \( \Delta \varepsilon = \frac{D}{d} \), where \( d \) — the diameter of a plastic print formed on a surface under the impact of a particle of a working environment of diameter \( D \).

Partial transition of deformation energy in the heat can be considered by means of the factor of accumulation of mechanical energy \( k_a \) which shows a share of reserved energy regarding all spent work \((k_a=0.2\div0.3)\). In this case:

\[ \Delta E_{pd} = k_a V_m 10^{-6} \sigma \frac{d}{D}. \] (7)

Taking into account (4-7), we receive:

\[ pdV = \Delta E_{es} + \Delta E_{pd} = V_m 10^{-6} \frac{\sigma^2}{2E} + k_a V_m 10^{-6} \sigma \frac{d}{D} = V_m 10^{-6} \left( \frac{\sigma^2}{2E} + k_a \sigma \frac{d}{D} \right). \] (8)

Experimental researches of the formation processes of the basic groups of the vibration mechanochemical coating have shown that for obtaining of VMCP of the first group, considerable power influences on working environment indenters are required, providing plastic deformation of the surface layer with the result that there is a penetration of dispersed microparticles of a material of a coating into a surface. As a consequence, we have a coating formation. In this case, the energy of elastic stresses can be neglected and the first summand in equation (8) is not to be considered. When obtaining VMCP of the second group, the defining role in their formation should belong both to elastic deformations, and to plastic ones. The former activate oxide films, the latter destroy them and strengthen adhesive links of the coating with the substrate. For VMCP formation of the third group, it is quite enough to provide mechanical work of indenters of a working environment at the level of elastic deformations as coating formation is carried out on the account of chemical reactions in the surface layer of a material, and the task of mechanical forces is to activate this process. At designing of VMCP technology, the mechanical component of the process of application of a demanded coating is controlled by the choice of a material and the indenters sizes of the working environment.

The third summand in equation (3) having dimensional energy is characterized by the contribution of non-mechanical reversible forces to accumulation of internal energy of the system, caused basically at VMCP by the course of material chemical and diffusion processes in the surface layer. This summand is presented in the form of the sum of the members containing chemical potentials of components, participating in the formation of a coating and describing chemical work spent on the change of the system structure, in a general view:
\[ A_{ch} = \sum \mu_i \Delta w_i \]  

(9)

If we consider chemical work as a work of an actually chemical reaction [7], then in non-equilibrium chemical reactions, processes in which some chemical forms of substance turn into other, chemical potentials define thermodynamic affinity - the integrated set of operating chemical forces characterizing transformation of the reaction to an equilibrium state. According to Lewis's method, the expression describing the change of chemical potential looks like

\[ \mu_i = \mu_i^0 + RT \ln a_i, \]  

(10)

where \( \mu_i \) – the standard chemical potential of the system component; \( \mu_i^0 = \frac{H}{N_a i} - H \) – component enthalpy; \( N_a \) – Avogardo’s number; \( a_i \) – relative activity of the component in the system; \( a_i = y_i c_i \); \( y_i \) – activity factors; \( c_i \) – component concentration.

From expression (10), it follows that activity, as well as chemical potential, is the measure of a tendency of the system component to turn into another phase. Herewith, chemical potentials are divided into two components - a constant one (standard) (depending only on temperature) and a variable one anyhow depending on the concentration of the substance in the system. At the same time, in work [8], it is shown that both chemical potentials and standard affinity can be presented through standard enthalpy and standard entropy of a reaction, in other words, through enthalpy change \( \Delta H^0 \) and entropy \( \Delta S^0 \) in a chemical reaction of the substances which are in standard conditions. Both those and other changes are defined, accordingly, by partial (and for pure substances as specific) mole enthalpies and entropies of participants of the reaction in standard conditions. This circumstance allows chemical reaction proceeding in the surface layer at VMCP and an increase of potential internal energy of local volume modified in the course of VMCP at the interface ‘coating – sublayer’ expressed through the change of free energy of Gibbs, kJ/mole:

\[ A_{ch} = -\Delta G^0 = -(\Delta H^0 - T \Delta S^0), \]  

(11)

where \( \Delta H^0 = \sum v_i h_{i}^0 \); \( \Delta S^0 = \sum v_i s_{i}^0 \); \( v_i \) – the stoichiometric factor; \( h_{i}^0 \) – enthalpy of the component mole; \( s_{i}^0 \) – mole entropy of the component.

The relation between enthalpic and entropic members in formula (11) at different temperatures defines the influence of temperature on the position of the reaction equilibrium. The opposite directedness of influence of enthalpic and entropic components on standard affinity is obvious, hence, on a direction of a chemical reaction as well. With the fall of the temperature, the role of the entropic component decreases essentially.

Taking into account (4, 8, 11), we have obtained the model uncovering the mechanism of mechanic-chemical synthesis of coating forming in the conditions of vibrational technological systems and defining the power condition of local microvolumes at the interface ‘coating – underlayer’ modified in the course of VMCP:

\[ TR \ln \left( \frac{1}{y_i} \right) + V_m 10^{-6} \left( \frac{\sigma^2}{2E} + k_\sigma \frac{d}{D} \right) - \Delta G^0 = U_0. \]  

(12)

Power model (12) accounts for the contribution to the process of VMCP formation of the surface layer of a raise of connected energy at the cost of the growth of entropy (the first summand), the increase of energy of elastic-plastic distortions of a crystalline grid as a result of mechanical action working environment indenter (the second summand), modifications of interior energy of the surface layer which was modified as a result of chemical interaction of contacting media. The role of each of them in kinetics of formation of classification groups of vibrational mecanochemical coatings according to the offered model (12) is schematically illustrated in figure 1, from which it is visible that the basic contribution of VMCP formation of the first group (figure 1a) to the process is made by a deformed summand monotonically growing in the course of time. VMCP formation of the second
group (figure 1b) is the result of deformation and chemical summands. During VMCP formation of the third group (figure 1c), the leading part belongs to a chemical component of the model.

![Diagram](image)

**Figure 1.** The diagram of energy accumulation in the local volume of the surface at the interface 'coating – substrate' by VMCP.

3. The energetic condition of VMCP durability provision.

The basic indicator of quality of any coating of metal applied to a metal surface is adhesion which characterizes the grasping durability between two materials, the connection occurrence between surface layers of two heterogeneous contacted substances. The basic performances of adhesion are energy of adhesion, the grasping durability and the force of adhesion. In work [9], devoted to the research of adhesion performances of contacting materials with coatings, it is established that adhesion energy and the grasping durability of a ‘coating-substrate’ are connected to each other by the following relation:

$$\tau_0 = \frac{1}{\sqrt{2\pi h}} \sqrt{E_a E},$$  

(13)

where, h- the thickness of a coating.

And the association between the force of adhesion and the grasping durability can be defined by the formula:

$$F_a = \pi \tau_0 r^2,$$  

(14)

where, r- the indenter radius at the top of a scleroscope needle.

Thus, having defined the energy of adhesion by one of the above-stated techniques in section 1, it is possible to calculate the grasping durability and the force of adhesion of the SP method by formulas (13, 14).

Quantitative performance of adhesion is adhesion work $W_a$ - the work necessary for reversible isothermal separation of two condensed phases given in the contact of the condensed phase on a square of the unit section. It is possible to present it in a following aspect:

$$W_a = E_a N,$$  

(15)

where, $E_a$ – the average energy of a communication unit providing adhesion of a modified on the basis of mechanochemical synthesis of the local microvolume at the interface of contacting environments; N- the number of links accounted for a contact square unit of a ‘coating-substrate’.
If it is necessary to equate the mole energy defining conditions of formation of the modified local microvolume at the interface ‘coating – underlayer’ to the average energy of a communication unit providing its adhesion \( U_0 = E_a \) on the basis of power model (12), we will receive an analytical dependence, providing coating generation of a material demanded by service conditions of durability on the surface:

\[
\text{TRIn} \left( \frac{1}{t_0} \right) + V_m 10^{-6} \left( \frac{\sigma^2}{2E} + k_a \sigma d_D \right) - \Delta G_0 = E_a \tag{16}
\]

The left side of equation (16) represented in the form of the time function is the VMCP kinetic equation which at \( t < t_p \), where \( t_p \) — the processing duration, describes the growth process of the internal energy of the forming coating. At moment \( t = t_p \), when plastic deformation becomes limitatory for the given material, that is, \( d = d_0 \), and the activity of system components reaches thermodynamic constant \( K \) (according to [1] \( \Pi_{i=1}^{m} (a_i)^{\gamma_i} = K \)), the forming process of the vibrational mechanochemical coating completes. Having expressed \( t_p \) we receive a generalized formula for the assessment of the VMCP process duration, providing VMCP formation:

\[
t_p = t_0 \exp \left[ \frac{E_a - V_m 10^{-6} \left( \frac{\sigma^2}{2E} + k_a \sigma d_D \right) + \Delta G_0}{RT} \right] \tag{17}
\]

4. Conclusion
The obtained power model (12) can be taken as a management principle of mechanochemical synthesis of the formation process of coatings in vibrational technological systems as it discovers the mechanism of influence of the technological environment and conditions of the VMCP course on kinetics of internal energy changes of local microvolumes of the surface layer modified on a surface during activating the strike-impulse impact of free moving (metallic or nonmetallic) indenters.

The offered analytical dependence (16) allows solving a number of optimizing problems connected with a choice of technological conditions of VMCP on quality maintenance of VMCP and operational properties of a surface of parts at a stage of technological preparation of manufacture.

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