

# Mathematical model for mechanical treatment of a reactive binary mixture passivated by inert material

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**Abstract.** A macroscopic mathematical model was built to theoretically study the mechanical treatment of a reactive solid mixture passivated by an inert substance milled from the walls of a mill chamber and grinding bodies. The model includes equations for the rate of chemical transformations, change in the mass of substances involved in the mechanical treatment, dynamics of excess energy in components and a reaction product. The process is considered to be isothermal. An equation is derived to obtain the function of the interphase, which is a superposition for the grinding of components and their passivation with an inert substance. The dynamics of the chemical transformation depth, the amount of a milled inert substance, the function of the interphase and reactivity of the mixture versus the mechanical treatment time are numerically calculated. The final fraction of the reaction product in the mechanically treated powder mixture is found as a function of the parameter characterizing the level of slagging of reagents with an inert substance. Based on the constructed calculation diagrams, it is shown that depending on the parameters determining the mechanical treatment, different modes that characterize either activation or passivation of chemical interaction in the reactive powder mixture were found.

## 1. Introduction

Mechanical treatment (MT) and mechanochemical synthesis, as a rule, are conducted in an energy-intensive mill in which the initial components of a mixture are ground and activated [1 - 9].

During mechanical treatment, chemical transformations are intensified due to the creation of a highly developed interphase between the components of the mixture, as well as due to the formation of a defective structure of the activated substance in which excess energy is accumulated.

At the same time, along with the activation processes during MT, passivation of components can take place due to the blockage of the reaction surface by the inert substance milled from the walls of a grinder and grinding bodies.

In most cases the presence of a milled inert substance is considered to be a negative factor. However, in certain circumstances, it is used for the obtaining of modified particles of complex precursors required for the synthesis of composite powders [10 - 12]. Here, a milled inert substance reduces the activity of the particles of precursors, which prevents the development of a premature chemical reaction in them. In practice, metallic, ceramic, organic (cellulose, polypropylene), amorphous (glass, sulfur) and other materials can be used as reactants, and iron [10 - 13] as an inert substance (modifier).



The purpose of this work is to study the effect of a milled inert substance on the mechanical treatment of a binary powder mixture, accompanied by the synthesis of a reaction product, using a built macroscopic mathematical model.

## 2. Computational approach

A binary powder mixture of components A and B, which form the product F during the single-stage irreversible synthesis reaction, is considered. Mechanical treatment of the powder mixture in the energy-intensive grinding device results in the formation of milled inert material I. In practice, both metal, ceramic, organic, amorphous and other materials can be used as reagents, and iron can be used as an inert substance (modifier).

### 2.1. Governing equations

In the isothermal approximation, mechanochemical synthesis caused by MT is described by the system of governing equations and relations [5, 14], which determine

- rate of chemical transformations:

$$\frac{d\alpha}{dt} = k(T)f(\alpha)F(S)k_0 \exp\left(-\frac{E}{RT}\right), \quad (1)$$

- dimensionless function that characterizes the change in the area of the reaction interphase between the reactants in the mixture:

$$F(S) \approx F(k^*)F(v_{AB}), \quad (2)$$

- rate of excess energy change in the reactants, the synthesis product and the inert substance:

$$\frac{d\varphi_i}{dt} = \Omega_i - \varphi_i m_i \exp\left(-\frac{U_i - \varphi_i}{RT}\right) \quad (i=A, B), \quad (3)$$

$$\frac{d\varphi_j}{dt} = \Omega_j - \varphi_j m_j \exp\left(-\frac{U_j - \varphi_j}{RT}\right) + \Omega_j^* \quad (j=A, F), \quad (4)$$

- change in the mass of substances A, B, I, F during chemical transformations:

$$m_A = V_0 \rho_0 (1-\alpha) c_0, \quad m_B = V_0 \rho_0 (1-\alpha) (1-c_0), \quad m_I = V_0 \rho_0 K t, \quad m_F = V_0 \rho_0 \alpha, \quad (5)$$

- dynamics of the volume concentrations of components A, B, I, F in the powder mixture:

$$v_i = \frac{m_i / \rho_i}{m_A / \rho_A + m_B / \rho_B + m_I / \rho_I + m_F / \rho_F} \quad (i = A, B, I, F). \quad (6)$$

In the relations (1) - (6) the notations were used as follows:  $t$  is time;  $T$  is temperature;  $\alpha$  is conversion depth (ratio of the mass fraction of desired product F to the mass of the reaction mixture, without taking into account the mass of the inert material I, and to product F;  $k_0$ ,  $E=E_0-a_E[\varphi_{AC0}+\varphi_B(1-c_0)]$  are a pre-exponential factor and activation energy of chemical reaction with allowance for the effect of excess energy stored in the reactants;  $E_0$  is activation energy of chemical reaction in a non-activated system;  $R$  is the gas constant;  $f(\alpha)$  is the kinetic law of reaction (it is assumed that the rate of transformations is limited to the first-order chemical reaction:  $f(\alpha)=1-\alpha$ );  $c_0$  is the mass content of component A in the mixture of reactants;  $a_E$  is a coefficient;  $I_i$ ,  $m_i$ ,  $U_i$ ,  $a_i$  ( $i=A, B, I, F$ ) are the rates of accumulation of excess energy during the operation of the mill, pre-exponential factors, activation energy and coefficients;  $\Omega_i^*$ ,  $\Omega_F^*$ , are the rates of excess energy change in substances (I) and (F) due to the increase in their mass;  $\rho_i$  is the density of the  $i$ -th component;  $V_0$ ,  $\rho_0=\rho_A \rho_B / [\rho_A (1-c_0) + \rho_B c_0]$  are the initial volume and density of the condensed phase. Note that in experiments, the excess energy stored in structural defects can be

estimated through the broadening of X-ray diffraction peaks, considering the relative broadening to be proportional to excess energy.

### 2.1.1. Additional relations

The additional relations, which specify the parameters included in (1) - (6), were used for the mathematical model formulated above.

In the third equation (5) it was assumed that the mass of the inert substance that is formed by milling linearly depends on the time of mechanical activation with the coefficient of proportionality  $K$ . In turn,  $K$  depends on the capacity of the mill and the surface area  $S_\Sigma$  from which the inert substance is milled.

$$K = a_\Sigma W S_\Sigma,$$

where  $W$  is the capacity of the mill;  $S_\Sigma = S_b + n_m S_b$ ,  $S_b$  are the area of the internal surface of the drum;  $S_m$  is the surface area of a grinding body;  $a_\Sigma$  is a coefficient;  $n_m$  is the number of grinding bodies. The change in the value  $S_\Sigma$  during mechanical treatment is neglected. Then, the equations for calculating concentrations can be written as:

$$v_A = \frac{(1-\alpha)c_0}{1+Kt}, \quad v_B = \frac{(1-\alpha)(1-c_0)}{1+Kt}, \quad v_I = \frac{Kt}{1+Kt}, \quad v_F = \frac{\alpha}{1+Kt}. \quad (7)$$

Given the continuous increase in the mass of substance I, for the last term of equation (4) the ratio is written as

$$\Omega_I^* = \frac{d\varphi_I}{dt} = -\frac{\varphi_I}{v_I} \frac{dv_I}{dt} = \frac{-\varphi_I}{(1+Kt)t}. \quad (8)$$

Since the dynamics of excess energy in products is determined not only by its change due to activation and relaxation, but also by the possible transition of some amount of the excess energy from reactants to products during a chemical reaction, then the additional term in equation (4) responsible for this process can be given by

$$\Omega_F^* = \frac{d\varphi_F}{dt} = -\frac{1}{v_F} \left[ \varphi_F \frac{dv_F}{dt} + a_{A1} \varphi_A \frac{dv_A}{dt} + a_{B1} \varphi_B \frac{dv_B}{dt} \right], \quad (9)$$

where  $a_{A1}$ ,  $a_{B1}$  are coefficients.

It is assumed that the first term in equations (3) and (4), which is responsible for the rate of accumulation of excess energy in the components of the powder mixture, is proportional to the capacity of the mill and the volume fraction of the substance [14]:  $\Omega_i = W a_{li} / V$ , where  $V$  is the total volume of the activated system;  $a_{li}$  are coefficients. It is easy to see that with the above assumptions for the powder mixture:  $V = V_0(1+Kt)$ .

In relation (2) the parameter  $F(k^*)$  is a function that determines the change in the reaction surface due to grinding of reactants;  $F(v_{AB})$  is a function that determines the effect of the volume fractions of substances on the formation of the interphase between reactants A and B. In differential form  $F(k^*)$  can be represented as [15]:

$$\frac{dF(k^*)}{dt} = [1 - F(k^*)] k_s \frac{W}{V} = [1 - F(k^*)] k_s \frac{W}{V_0(1+Kt)}, \quad (10)$$

where  $k_s$  is a coefficient.

Denoting  $k^* = k_s W / V_0$  and integrating the above equation, the relation for  $F(k^*)$  takes the form:

$$F(k^*) = 1 - (1+Kt)^{-k^*/K}. \quad (11)$$

Here the parameter  $k^*$  has the meaning of the grinding rate constant. It is seen that in the absence of the milled inert substance, i.e. for  $K \rightarrow \infty$ , the formula

$F(k^*) = 1 - (1 + Kt)^{-k^*/K} = 1 - [(1 + Kt)^{1/Kt}]^{-k^*t} \rightarrow 1 - e^{-k^*t}$  (since it is known that if  $K \rightarrow \infty$ , then  $(1 + Kt)^{1/Kt} \rightarrow e$ ) coincides with the formula for the surface dynamics of the ground particles obtained in [17].

$F(v_{AB})$  physically characterizes the probability of the formation of interfaces between A and B in the system, in this case, containing four substances: A, B, I, F. In the first approximation, by analogy with [16], the function takes the form:

$$F(v_{AB}) \approx K_{AB} v_A v_B, \quad (12)$$

i.e. the probability of formation of a reaction interphase is proportional to the product of the specific volumes of reactants ( $K_{AB}$  is a coefficient). Then, the function describing the dynamics of the interphase can be represented as

$$F(S) \approx \left[ 1 - (1 + Kt)^{-k^*/K} \right] K_{AB} \frac{(1 - \alpha)^2 c_0 (1 - c_0)}{(1 + Kt)^2}. \quad (13)$$

### 2.1.2. Initial conditions

Primary agglomerates consisting of mixture components, physicochemical evolution of which is described by the above equations, are formed at the initial stage of mechanoactivation. Neglecting the change in the determined values at the stage of formation of primary agglomerates, the initial conditions are given by

$$t = 0: \quad \alpha = 0; \quad \varphi_i = 0. \quad (14)$$

Thus, the system of equations (1) - (5) with supplementary relations (6) - (13) and initial conditions (14) form a mathematical model of the mechanochemical synthesis of fine powders with allowance for the presence of an inert substance.

## 3. Computational results

In order to reduce the number of parameters, select the governing parameters and simplify analysis and calculations, dimensionless quantities are introduced as follows:  $\tau = tk_0 \exp(-E_0/RT) = tK(T)$ ,  $\tau_{MT} = t_{MT}k(T)$ ,  $\psi_i = \varphi_i/RT$  are current time, mechanical treatment time and excess energy;  $\Delta_i = Wa_i/V_0RTk(T)$  is the rate of accumulation of excess energy in component i;  $\psi_E = \varphi_E/RT$  is the proportion of excess energy affecting the activation energy of chemical reaction;  $\mu_i = m_i(T)/k(T)$  is the parameter that determines the ratio between the characteristic times of relaxation and chemical reaction;  $\varepsilon_i = U_i/E_0$  is a parameter expressing the ratio of the activation energy of chemical reaction to that of excess energy relaxation;  $K^* = k^*/k(T)$  is a grinding rate constant;  $z = Kk(T)$  is the parameter that determines the ratio between the characteristic rates of the formation of an inert substance and chemical reaction;  $i = A, B, I, F$ .

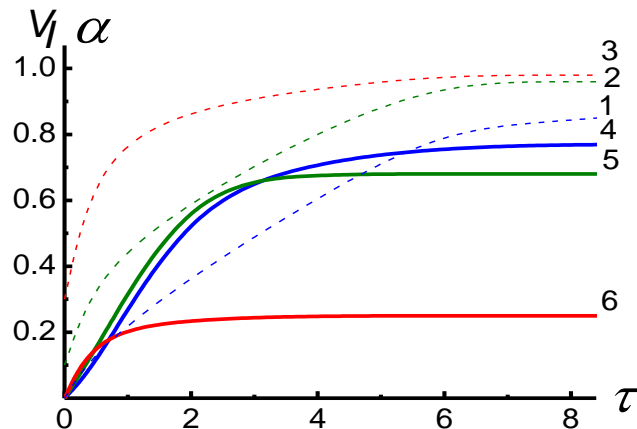
A new parameter  $z$ , not used previously in such models, is introduced in the macroscopic model of mechanochemical synthesis presented above. In the paper, the value  $z$  is varied from 0 to values at which the effect of the milled inert substance on the process of mechanosynthesis becomes significant.

It is considered that  $\Delta_i = \Delta$ . Note that the parameters  $\Delta$  and  $z$  are proportional to each other, since their joint change is due to varying the capacity of the mill. Therefore  $\Delta = \nu z$ , where  $\nu = a_i/V_0RTk(T)a_{\Sigma}S_{\Sigma}$ . In an experiment, the parameter  $\nu$  can be varied, for example, by changing the volume of the milled condensed phase  $V_0$ , as well as through the area of the internal surface of the mill drum  $S_{\Sigma}$ .

The equations written above were numerically integrated using the author's numerical code and the Euler scheme of the first order accuracy. The stability of the difference scheme was provided by limiting the time step in accordance with the condition  $\Delta t < 2\theta_i/|\theta_{i+1} - \theta_i|$ , where  $\theta_i, \theta_{i+1}$  are the function values in the previous and subsequent time steps. A quantitative analysis of the model was performed using dimensionless variables and parameters. The validity of the results obtained was confirmed by the conservation law of mass balance involved in the mechanochemical treatment and synthesis of the

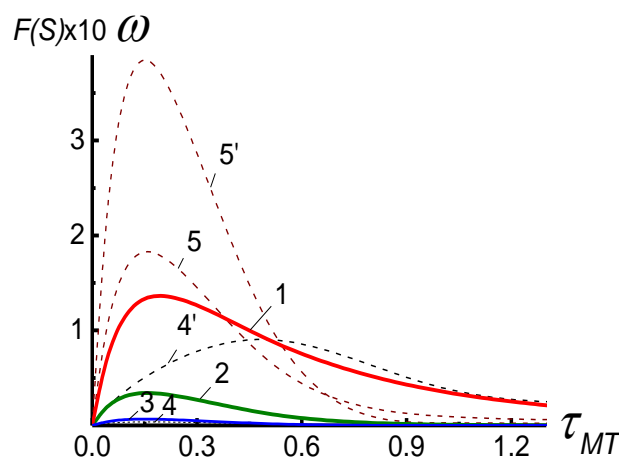
system (the computation error did not exceed 1%). In general, the behavior of the calculated curves corresponds to the experimental data available in the scientific literature.

We emphasize that this problem was solved in the isothermal approximation. The latter takes place during mechanical treatment of systems with a low thermal reaction effect and a cooled mill body. Under such conditions, the temperature of mechanochemical treatment is close to the ambient temperature. Figure 1 shows the kinetic dependences of the milled (curves 1–3) inert substance and the depth of chemical transformation (curves 4–6) for different values  $V_I$ ,  $\alpha$  of the parameter  $z$ .



**Figure 1.** Kinetic dependences of the milled inert substance (curves 1 - 3) and the depth of chemical transformations (curves 4 - 6) for  $S_0=0.001$ ,  $z=1$  (1),  $z=10$  (2),  $z=100$  (3),  $K^*=16000$ ,  $\nu=12.7$ ,  $\psi_0=0$ ,  $\varepsilon_i=0.35$ ,  $a_F=3$ ,  $c_0=0.6$ .

It can be seen that with increasing  $z$  the formation rate of the inert substance increases resulting in a sharp decrease in the depth of chemical transformation in the powder mixture subjected to mechanical treatment. The latter is explained by a decrease in the interphase due to blocking by the inert substance (Fig. 2, curves 1 - 3).



**Figure2.** Dimensionless interphase area (curves 1–3) and the reactivity of the mixture (curves 4, 4', 5, 5') as a function of the mechanical treatment with allowance for the inert substance  $z=10$  (curves 4 and 5) and without the inert substance ( $z=0$ , curves 4' and 5') for different values of the parameter  $\nu$ : 4, 4' - 1.27; 5, 5' - 12.7. The other parameters correspond to the captions to Fig. 1.

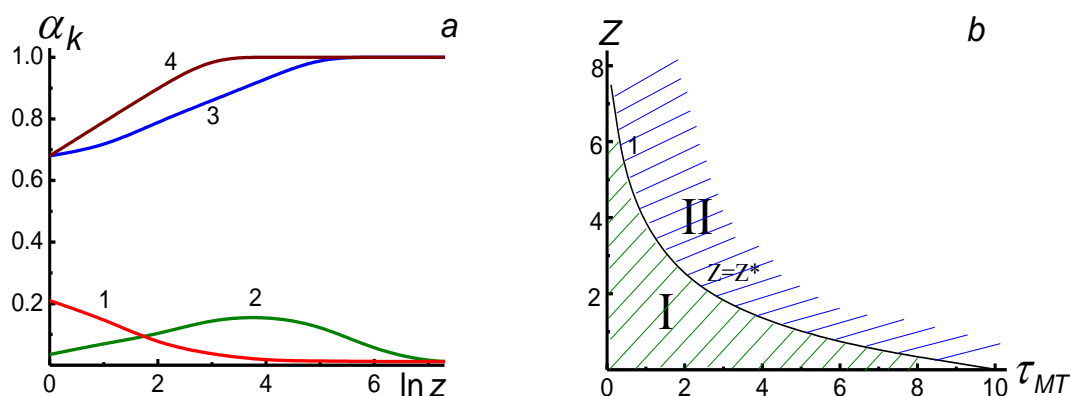
The effect of mechanical treatment time on the rate of mechanochemical synthesis is shown in Fig. 2 (curves 4, 4', 5 and 5'). It can be seen that firstly the magnitude  $\theta$  increases both due to an increase in the interphase during the grinding of particles and due to an increase in the excess energy in the mixture components. However, during further mechanical treatment, the interphase is blocked by synthesis products and its reactivity decreases noticeably. Moreover, considering the presence of the inert substance, along with the synthesis products, contributes to blocking the interphase by the inert substance and decreases intensively the value  $\theta$ .

Fig. 3 (a) shows the function of the final depth of transformation  $\alpha_k$  versus the parameter  $z$  for different values  $\nu$  and the mechanical treatment time  $\tau_{MT} = \text{const}$ . It can be seen that, depending on the value  $\nu$ , different modes of modification of the powder processed in the mill can take place. For small values  $\nu$ , only passivation of particles is observed with increasing the formation rate of the inert substance, since here  $d\alpha_k/dz < 0$  (curve 1). For average values  $\nu$  (curve 2), the increase in  $z$  leads to activation ( $d\alpha_k/dz > 0$ ) on a small segment, and then, with a further increase in the formation rate of the inert substance, passivation ( $d\alpha_k/dz < 0$ ) takes place. For relatively large values of the parameter  $\nu$  with increasing  $z$ , activation of particles is observed and the depth of chemical transformation noticeably increases in them (curves 3 and 4). A slight decrease in the activation of product takes place only for large formation rates of the inert substance and depths of chemical transformation.

A typical “mechanical treatment time ( $\tau_{MT}$ ) – formation rate of the inert substance ( $z$ )” diagram demonstrating different scenarios of the mechanical treatment of the reactive mixture is shown in Figure 3 (b). Line 1 is the locus of the parameters ( $\tau_{MT}, z$ ) at which the condition:  $z = z^*$  is met.

In region I, with an increase in mill power, the reactivity of the mixture increases. Here, the interphase growth rates during mechanochemical treatment, as well as the increase in the excess energy content in the reagents prevail over the passivation rate of particles by an inert substance and contribute to the intensification of chemical interaction.

In region II, on the contrary, the passivation rate of reagent particles outstrips the rate of their mechanical activation, as a result of which the reactivity of the powder mixture decreases with increasing the mill power.



**Figure 3.** a) Final depth of chemical transformations as a function of the parameter  $z$  for different values  $\nu$ ,  $\tau_{MT}$ : 1 ( $\nu=1.27$ ,  $\tau_{MT}=1$ ), 2 ( $\nu=12.7$ ,  $\tau_{MT}=0.1$ ), 3 ( $\nu=127$ ,  $\tau_{MT}=0.1$ ), 4 ( $\nu=1270$ ,  $\tau_{MT}=0.1$ ). b) Diagram « $z - \tau_{MT}$ » for  $\nu=12.7$ . The other parameters correspond to the captions to Fig. 1.

Based on this type of diagrams, depending on the purpose of mechanochemical synthesis, it is possible to determine the optimal modes of the process. If it is necessary to obtain a large number of highly active particles of the final product by mechanical treatment, then this case will correspond to the area of mechanical treatment I. Such reactive particles can be used in the future for the synthesis of materials outside the mechanical activator or for the manufacture of catalysts, nanocomposites, etc. For example, for the obtaining of modified particles of precursors, the optimal modes are in that part of

region II, in which the conversion depth in the particles does not exceed the specified one, and the degree of modification by the inert substance is significant. Such modified particles with an increased wear resistance in various corrosion media can be used to create composites, hardening coatings, etc.

The determination of effective kinetic constants that can be found by the inverse problem method using the constructed mathematical model is of great practical importance. A new parameter, the coefficient  $K$ , which characterizes the milling rate of an inert substance I, can be estimated in the third relation in (7), experimentally determining the fraction of the inert substance  $v_I$  depending on the mechanical treatment time  $t$ .

### Conclusion

1. A macroscopic mathematical model was built to study mechanochemical synthesis in a binary powder mixture subjected to mechanical treatment in an energy-intensive mill with allowance for the inert material milled from the walls of the mill chamber and grinding bodies.
2. The conditions for the activation and passivation of particles of a powder mixture subjected to mechanical treatment were found, contributing either to an increase in the reactivity of particles, or to its reduction by blocking the interphase by milled inert material.
3. Various mechanochemical synthesis modes differing in the degree of modification of small-sized powder particles and completeness of chemical transformations in them were found depending on the parameters determining the process (mill capacity, mechanical treatment time, mass of the mixture, size of the internal surface of the mill chamber).

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### Notifications

MT - Mechanical treatment