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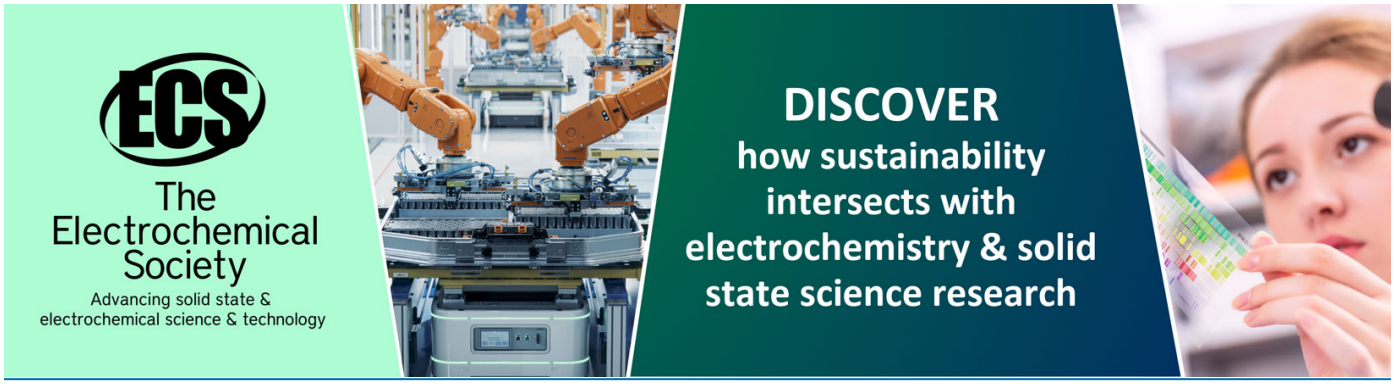

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Mathematical model of the formation of mechanocomposite particles during the mechanical treatment of a powder mixture

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Abstract. A mathematical model of the formation of layered mechanocomposites during the grinding of a binary mixture in an energy-intensive mill is built and studied. Dynamics of structural parameters of the binary mixture (the external and internal surface area of particles, the rate of particle agglomeration into mechanocomposites) as a function of the mechanical treatment time is investigated. Analytical relations are obtained to develop a technique for determining the kinetic constants using the inverse method.

1. Introduction

One of the effective methods to accelerate chemical transformations in powder mixtures is their intensive mechanical treatment. In practice, planetary mills are most often used for this purpose. During mechanical treatment, along with the grinding of powders, an interphase necessary for chemical interactions is formed. The interphase is formed by "spreading" one of the reagents on the other reagent in the places of their frictional contact. During mechanical treatment, such layered microcomposites are continuously ground and new microcomposites are formed with a more complicated internal structure, in which reaction products may occur. The development of this process reduces the size of individual layers of reagents, namely the heterogeneity scale that determines the characteristic time of mass transfer of reagents to each other. In the limiting case, the heterogeneity scale may become so small that the slowest (limiting) stage of chemical transformations can move from the mass transfer of reactants to each other to chemical reactions.

Simultaneously with the grinding and formation of microcomposites, additional structural defects that accumulate excess energy are created in the components of the mixture. In the macroscopic approximation, some amount of this energy reduces the activation barrier of chemical interactions.

Depending on the intensity and time of mechanical treatment, chemical transformation can occur in the mill. In this work the obtaining of mechanocomposite particles consisting of the agglomerated mixture components is considered, in which the reaction product is either absent, or present in an insignificant or predetermined amount. Such particles (precursors) are used to create new substances and materials by different methods, including technological combustion methods [1 – 9].

The rate of chemical transformation, physical and chemical, and mechanical properties of mechanocomposites are mainly determined by their structure, including a layer structure that is characterized by the thickness of alternating inner layers consisting of different components in mechanocomposites [10].

The purpose of this work is to build a mathematical model of the formation of mechanocomposites and evaluate the kinetics of chemical transformations.

2. Computational approach

A two-component mixture of A and B powders which during mechanical treatment are ground and agglomerate into mechanocomposites AB. Let component A be more solid, and component B is ground easier.

The constitutive parameters to be theoretically defined in this paper are: particle size and volume fractions of initial components and obtained mechanocomposites, external specific surface, and interphase surface in mechanocomposites, which characterizes the degree of its lamination.

Let us assume the following assumptions:

- components of the mixture, including formed heterogeneous agglomerates, are ground independently of each other;
- regardless of the nature of components, their agglomeration is described by similar phenomenological dependencies using the effective parameters characterizing the agglomeration rate and rheological properties of the mixture, which are assumed to be constant and independent of the mechanical treatment conditions;
- particles of initial components and agglomerates have a shape which can be described by a sphere that is equivalent to the surface of particles and does not change during mechanical treatment;
- densities of all substances are assumed to be equal;
- mechanical treatment of the mixture is considered to be isothermal.

Agglomerates are formed in two ways: from heterogeneous particles of the A and B mixture (the first type of agglomeration) and due to the addition of initial mixture particles to the existing agglomerates (the second type). In this case, the system of equations describing the dynamics of grinding and formation of mechanocomposites from the mixture of A and B powders subjected to mechanical treatment can be written in the form [11]

$$\frac{\mathrm{d}s_i}{\mathrm{d}t} = \left(1 - \frac{s_i}{s_{mi}}\right) k_i \ (i = A, B), \qquad (1)$$

$$\frac{\mathrm{d}(s_{AB})}{\mathrm{d}t} = (s_{mAB} - s_{AB}) \frac{k_{AB}}{s_{mAB}} + \left[\frac{s_A s_B \mu_A \mu_B (\lambda \mu_A + \mu_B)}{\mu_{AB} (s_A \mu_B + \lambda s_B \mu_A)} - \frac{s_{AB} (\mu_A + \mu_B)}{3} \right] q \,, \qquad (2)$$

$$\frac{\mathrm{d}\mu_i}{\mathrm{d}t} = -\left[\mu_i^2 \mu_j + \mu_i \mu_{AB} (\mu_A + \mu_B)\right] \frac{\lambda q}{\lambda \mu_A + \mu_B} \ (i, j = A, B;\ i \neq j). \qquad (3)$$

Equations (1) and (2) determine the change in the specific surfaces of initial materials and mechanocomposites, and equation (3) is the ratio for the rate of change in the volume fractions of A and B during agglomeration. In (1) - (3) the notations are used as follows: t is time; V_i, $s_i=S_i/V_i$, S_i are the volume, specific and absolute surfaces of the i-th component; s_{mA}, s_{mB}, s_{mAB} are the maximum values of specific surfaces; V is the volume of the mixture; $\mu_i=V_i/V$ is the relative volume of the i-th component in the mixture; $k_A=k'_AW/V$, $k_B=k'_BW/V$, $k_{AB}=k'_{AB}W/V$; W is the power of the mill; k'_A, k'_B, k'_{AB} are coefficients. The radius of the A, B, AB particles is related to the specific surface by the following ratios: $r_A=3/s_A$, $r_B=3/s_B$, $r_{AB}=3/s_{AB}$, $q=q'W/V$ is the agglomeration rate constant; q' is a coefficient that depends on the physical and chemical properties of the components involved in agglomeration. The coefficient λ takes into account the difference in the rheological properties of components A and B. Since B is chosen as the component that is easier subjected to grinding, the value λ varies from 0 (agglomerates of heterogeneous particles are not formed) to 1 (equal participation of both components in the formation of agglomerates in the limiting case with identical rheological properties).

The relative volumes of the mixture components are related by the ratio as follows

$$\mu_A + \mu_B + \mu_{AB} = 1. \qquad (4)$$

Initial conditions:

$t=0$: $\mu_A=\mu_{0A}$, $\mu_B=\mu_{0B}$, $\mu_{AB}=0$, $s_A=s_{0A}$, $s_B=s_{0B}$, $s_{AB}=0$. (5)

The volume fractions of components A and B in mechanocomposites are determined by the formulas

$$v_A=\frac{\mu_{0A}-\mu_A}{\mu_{AB}},\ v_B=\frac{\mu_{0B}-\mu_B}{\mu_{AB}}. \quad (6)$$

A change of the interphase between the mixture components takes place due to the agglomeration of existing particles of mechanocomposites and the formation of new particles during the agglomeration of the components A and B, the formation of which is described in detail in [11]. Based on this fact, the equation of the interphase velocity in mechanocomposites can be given by

$$\frac{\mathrm{d}F(S)}{\mathrm{d}t}=\frac{\partial F(S)}{\partial t}+\frac{\partial F(S)}{\left|\partial(\mu_A+\mu_B)\right|}\left|\frac{\mathrm{d}(\mu_A+\mu_B)}{\mathrm{d}t}\right|. \quad (7)$$

The growth rate of the internal specific interphase $F(S)$ without the addition of new particles (the first term in equation (7)) is assumed to be proportional to the agglomeration rate I_a and depends on the probability of formation of the interphase $F(v_{AB})$ between components A and B in a single agglomeration. Based on these facts, the relation can be written in the form

$$\frac{\partial F(S)}{\partial t}=F(v_{AB})I_a, \quad (8)$$

where $F(v_{AB})=k_{AB}v_Av_B$ (the probability of formation of the interphase between A and B is assumed to be proportional to the product of their volumes in an agglomerate [11]), k_{AB} is a coefficient. In (8) the rate of agglomeration of particles subjected to mechanical treatment is proportional to the surface of the particles (the larger the surface, the higher the probability of their agglomeration)

$$I_a=K_aS, \quad (9)$$

where K_a is the coefficient of agglomeration, $S=s_{AB}/s_{mAB}$. The second term in (7) describes the change of the internal surface of the agglomerates due to the addition of new particles which form the interphase that is not developed yet; therefore, its value will be neglected as compared to the value of the function $F(S)$.

Then

$$\partial F(S)=\frac{F(S)\mu_{AB}}{\mu_{AB}+\left|\mathrm{d}(\mu_A+\mu_B)\right|}-F(S)=\frac{-F(S)\left|\mathrm{d}(\mu_A+\mu_B)\right|}{\mu_{AB}}. \quad (10)$$

Using (8) - (10), equation (7) can be rewritten as follows

$$\frac{\mathrm{d}F(S)}{\mathrm{d}t}\approx K_{AB}v_Av_B\frac{s_{AB}}{s_{mAB}}-\frac{F(S)}{\mu_{AB}}\left|\frac{\mathrm{d}(\mu_A+\mu_B)}{\mathrm{d}t}\right|, \quad (11)$$

where $K_{AB}=k_{AB}K_a$. The thickness of the layer in the layered structure of mechanocomposite is given by

$$d=\frac{1}{F(S)}, \quad (12)$$

where $d=r_*/r_{mAB}$, r_* is the thickness of the layer.

The system of equations (1) - (6), (11) and (12) describes the dynamics of the formation of mechanocomposites, as well as their structural transformations during the mechanical treatment of the powder mixture.

3. Computational results

The dynamics of the formation of mechanocomposites from weakly reacting powders was studied in detail in [11]. In this work, to simplify calculations and obtain analytical dependencies, the stage of initial formation of agglomerates can be neglected as compared to the duration of mechanical treatment, therefore:

$\mu_A \approx 0$, $\mu_B \approx 0$, $v_A = \mu_{0A}$, $v_B = \mu_{0B}$.

Integrating equation (3), the relation is obtained for the specific surface area of the mechanocomposite

$$s_{AB} = s_{mAB}(1 - e^{-Kt}), \quad (13)$$

where $K = r_{mAB} k_{AB}$. Considering the above simplifications, equation (13) is substituted into equation (11) and integrated to obtain the relation for the specific interphase surface in the mechanocomposite

$$F(S) \approx K_{AB} \mu_{0A} \mu_{0B} \left(t + \frac{e^{-Kt}}{K} - \frac{1}{K} \right). \quad (14)$$

Relation (14) can be simplified. For the small mechanical treatment time that is much smaller than the characteristic grinding time ($t << 1/K$), formula (14) is expanded into a Taylor series at a point t=0

$$F(S) \approx K_{AB} K \mu_{0A} \mu_{0B} \frac{t^2}{2}. \quad (15)$$

In the case when the mechanical treatment time greatly exceeds the characteristic grinding time, in (14) it is assumed that $t >> (1/K, e^{-Kt}/K)$ and the relation can be rewritten in the form:

$$F(S) \approx K_{AB} \mu_{0A} \mu_{0B} t. \quad (16)$$

The equations written above were numerically integrated according to 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 θ_i, θ_{i+1} are the function values in the previous and subsequent time steps.

Figure 1 shows the dynamics of structural transformations of mechanocomposites subjected to mechanical treatment in the energy-intensive mill. It is seen that with an increase in the mechanical treatment time the external specific surface of particles increases due to grinding, approaching the limiting value (curve 1). At the same time, monotonous and almost linear growth of the interphase in mechanocomposites is observed (curve 2) during the grinding-agglomeration stages. The calculation of the value *F(S)* by the approximate formula (15) (line 2') well approximates curve 2 for the small mechanical treatment time. Increasing the duration of the mill operation and, accordingly, the growth of *F(S)*, this relation is more precisely approximated with the straight line 2'' calculated by the formula (16).

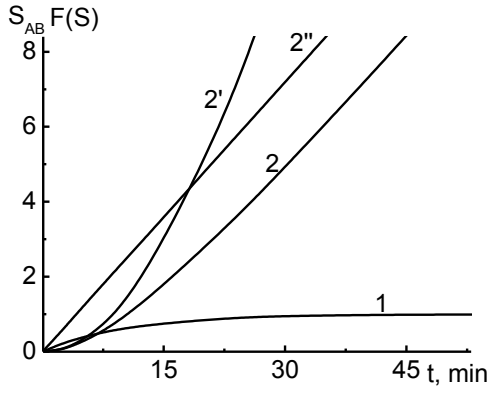

Figure 1. Change of the external (1) and reaction (2) specific surfaces of the mechanocomposite particle during grinding. Lines 2 'and 2' 'are an analytical calculation of the reaction surface *F(S)* using formulas (15) and (16), respectively.

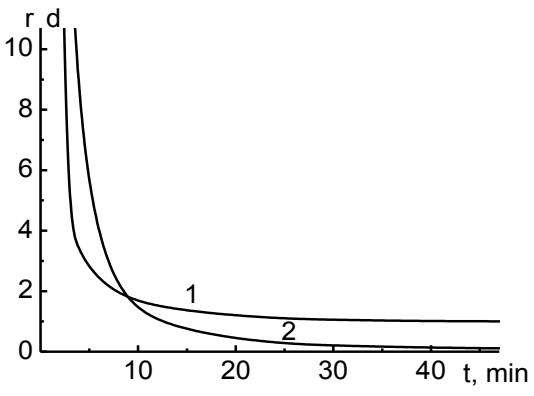

Figure 2. Particle size (1) and thickness of the layers of the mechanocomposite (2) during the grinding of a binary mixture.

With an increase in the mechanical treatment time, the size of mechanocomposites decreases to the limiting value (curve 1, Fig. 2). At the same time, the thickness of the inner layers of mechanocomposites monotonously decreases according to the hyperbolic law (curve 2, Fig. 2).

It should be noted that even after the grinding limit is reached and the particle size and the internal surface area do not change, the internal structure becomes more complicated and the interphase and the uniform distribution of components in mechanocomposites grow. Such evolution of the structure of a powder mixture subjected to mechanical treatment is in qualitative agreement with the experimental data given in [11, 12] and the works cited in them.

For practical applications, the evaluation of effective kinetic constants which describe the change of the structure of mechanocomposites is essential. Constants can be determined using experimental data and a mathematical model of the process (the inverse method). Thus, relation (14) for a specific interphase surface can be used to solve the inverse problem to determine a constant K_{AB}. In this case, the thickness of the layer d in the structure of the obtained mechanocomposite is determined from the experiment at the time t, and the required parameter is found from (14) using (12)

$$K_{AB} = \frac{1}{d\mu_{0A}\mu_{0B}\left(t + e^{-Kt}/K - 1/K\right)}. \quad (17)$$

Formula (17) is used, provided that the grinding parameter K is a known value. Otherwise, the parameters K_{AB} and Kcan be determined from relations (15) and (16). For long grinding, K_{AB} is found from (16)

$$K_{AB} \approx \frac{1}{d\mu_{0A}\mu_{0B}t} \ (\mathrm{t} >> 1/\mathrm{K}). \quad (18)$$

Then, knowing K_{AB} at the small mechanical treatment time, the grinding parameter is determined from (15)

$$K = \frac{2}{dK_{AB}\mu_{0A}\mu_{0B}t^2} \ (t << 1/K). \quad (19)$$

Thus, knowing the kinetic parameters K and K_{AB}, as well as the total time of mechanical treatment of the mixture t_{MO}, the value of the interphase $F(S)$ in the layered mechanocomposites can be determined. The latter parameter is important for determining the rate of chemical transformations in mechanocomposites. The interphase significantly increased during mechanical treatment, along with a decrease in the effective activation energy, accelerates the reaction rate and decreases the temperature of initiation of thermal explosion and combustion of the mechanically treated powder mixture.

Chemical transformation in the mechanically treated mixture can be used as a test of the proposed model. For this purpose, kinetic parameters should be determined from relations (17) - (19) for a particular system. Then $F(S)$ is determined from the chemical conversion equation and the numerical solution of the problem is compared with the experimental data (α is the conversion depth (mass fraction) of the final product, f(α) is a kinetic law, $K(T)$ is a chemical reaction rate constant).

$$\frac{d\alpha}{dt} = f(\alpha)K(T)F(S), \quad (20)$$

In this case, in the experiments the samples with a pre-normalized structure should be used to eliminate the effect of excess energy stored in structural defects on the reaction parameters.

4. Conclusion

1. A mathematical model of the formation of the external and internal structure of mechanocomposites during the mechanical treatment of a binary mixture in a grinding mill was built and numerically and analytically studied. The model can calculate the constitutive parameters of the process: volume

fractions of initial components and obtained mechanocomposites, particle size of components and mechanocomposites, external and internal (interphase) surface of particles, and the lamination degree of mechanocomposites.
2.The dynamics of the process was described. It was shown that the increase in the mechanical treatment time led to the decrease in the size of mechanocomposite particles and the increase in the uniform distribution of initial components.
3 Analytical relations characterizing the change in the external and internal surfaces of the particles of mechanocomposites as a function of the mechanical treatment time were obtained. Based on the obtained formulas and the inverse method, an algorithm was proposed for determining the kinetic grinding and agglomeration constants characterizing the formation of mechanocomposites.

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