

# Theoretical and Experimental Investigation of Mechanochemical Synthesis of Nanoparticles by Means of Dilution with the Final Product

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## Abstract

Theoretical and experimental investigation of the solid-phase mechanochemical synthesis of nano-sized target product on the basis of dilution of the initial powder mixture of reagents with another product of the exchange reaction was carried out. Optimal molar ratios of the mixture components providing shock-friction contacts of reagent particles and excluding aggregation of nano-sized particles of the target reaction product were calculated basing on the three-modal particle size distribution. A deduction of the kinetic equation for the mechanochemical synthesis of nanoparticles by means of dilution is presented. The necessary time of mechanical activation (MA) for the exchange reactions to process till completion is calculated using this equation. The obtained theoretical results agree with the available literature data and with the results of experimental investigation of the kinetics of mechanochemical synthesis of nano-sized target product TiCl according to the exchange reaction  $2\text{NaCl} + \text{Ti}_2\text{SO}_4 + z\text{Na}_2\text{SO}_4 = (z + 1)\text{Na}_2\text{SO}_4 + 2\text{TiCl}$  for the optimal value of dilution parameter  $z = z_1^* = 11.25$ . A number of specific features of this reaction are established. Comparing the kinetic parameters obtained for mechanochemical synthesis of TiCl with those for theoretically investigated exchange reaction  $\text{KBr} + \text{TiCl} + z\text{KCl} = (z + 1)\text{KCl} + \text{TiBr}$  for  $z = z_1^* = 13.5$ , experimental estimation of the mass transfer coefficient was carried out for the first time and the dynamics of changes in the size of nanoparticles depending on the time of MA was established for a ball planetary mill AGO-2.

## INTRODUCTION

Synthesis of nanoparticles by means of mechanical activation (MA) is one of the important methods from the practical point of view [1–3]. As a rule, the apparatus arrangement of these technologies involves ball mills [1]. The results of mechanochemical synthesis of nanoparticles in the area of investigation of the exchange mechanochemical reactions with an excess of one of the final products (diluent) were summed up in [3]. For a number of investigated systems, nanocrystals of the target product with grain size  $\sim 10$  nm were obtained in the matrix of soluble diluent.

Removal of the matrix by washing it out with proper solvents allowed one to obtain a separate phase of nanoparticles at the final stage. The use of a diluent followed two aims: to exclude ignition of combustion reaction in the mechanochemical reactor [1, 4] and to decrease the volume fraction of nanoparticles thus preventing their agglomeration [3, 5]. However, the mass, volume or molar ratio of reagents to one of the reaction products, namely diluent, in the initial powder mixture is to be chosen only experimentally [5–7], similarly to the conditions of MA of the prepared mixture (geometric and kinematic parameters of the mechanochemical reactor, comparative

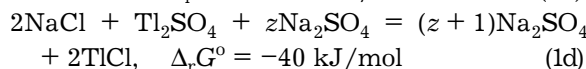
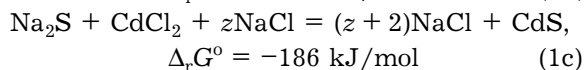
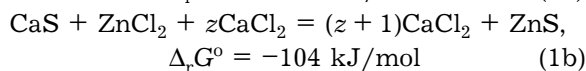
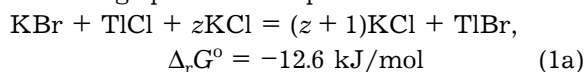
characteristics of the milling bodies and the material under treatment, kinetic parameters, such as time of MA, *etc.*). In the present paper we make the first attempt to describe this method theoretically obtaining numerical estimations.

It should be noted that the exchange chemical reactions in stoichiometric mixtures of the ionic crystal salts in planetary mills proceed at very high rate [8]. For example, reaction  $\text{NaNO}_3 + \text{KCl} = \text{KNO}_3 + \text{NaCl}$  in EI 2×150 planetary mill proceeds till completion within MA time  $\tau \approx 15$  min [9]. Because of this, it was necessary to establish: a) how the dilution of the initial stoichiometric mixture with one of the final reaction products affects the rate of MA exchange reaction; b) the mechanism of the exchange reaction with the dilution by the final product; c) what is the morphology of the resulting particles of the final products formed in the exchange reaction and how it changes during time  $t$ . It is evident that with the addition of a large amount of the diluent the exchange process should not only slow down but also cease completely after the contacts between the initial reagents in the mechanically activated mixture are exhausted. However, this is not observed experimentally [5–7]. Therefore, a mass transfer mechanism exists in a mechanochemical reactor; this mechanism can be connected only with the mobile milling bodies. In this case, the particle size of the final product should change from subnanometer scale to the micrometer one, which is characteristic of the reactions in the stoichiometric mixtures of salts [8]. Because of this, an optimal time of MA  $t$  should exist which would provide both the completeness of the exchange reaction and obtaining nano-sized particles of the target reaction product in the diluent matrix. Investigation in this aspect of the formulated problems has been carried out for the first time.

#### PROBLEM FORMULATION AND SOLVING PROCEDURES

Let us consider classical mechanochemical reactions of obtaining nano-sized products ( $\text{B}_h\text{D}_m$ ,  $\text{TlBr}$ ,  $\text{ZnS}$ ,  $\text{CdS}$ ) in the form  $km\text{A}_h\text{D}_l + h\text{B}_k\text{C}_m + z\text{A}_k\text{C}_l = (z + hm)\text{A}_k\text{C}_l + lk\text{B}_h\text{D}_m$  (1)

and using specific examples:



where  $h$ ,  $k$ ,  $l$ ,  $m$  are integer numbers while  $z$  is any positive number. The details of realization of the reactions like (1) for obtaining zinc sulphide nanoparticles (1b) [6] and quantum dots of cadmium sulphide (1c) [7] and others were described in [3, 5–7]. Unfortunately, the majority of reagents in reactions (1b), (1c) –  $\text{CaS}$ ,  $\text{ZnCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{Na}_2\text{S}$  and  $\text{CdCl}_2$  – are hygroscopic; the sulphates in (1d) are low-symmetrical, so their mechanical properties are not investigated. Thus, a hypothetical reaction (1a) is investigated theoretically. The problem includes numerical estimation of the value  $z = z^*$  which determines the optimal conditions for obtaining nanometer-sized particles of  $\text{B}_h\text{D}_m$  compound by means of dilution with the product of mechanochemical reaction  $\text{A}_k\text{C}_l$ . Reaction (1a) combines both ionic ( $\text{KBr}$ ,  $\text{KCl}$ ) and covalent ( $\text{TlCl}$ ,  $\text{TlBr}$ ) reagents and product; their physicochemical characteristics have been thoroughly investigated since these compounds are materials for infrared spectroscopy (Table 1). All the results of numerical modeling are presented for MA of this reaction as an example. However, practical realization of reaction (1a) is hindered by the fact that the compounds with poor solubility in water are present both in the left-hand part ( $\text{TlCl}$ , 0.35<sup>25</sup> °C, mass %) and in the right-hand one ( $\text{TlBr}$ , 0.05<sup>25</sup> °C). Because of this, we carried out the experimental test of the obtained theoretical results for the realization of reaction (1d) in the planetary mill AGO-2 as an example. This reaction is similar to (1a) and corresponds to the conditions of nanoparticle synthesis by dilution with the final product as established in [3, 5–7]. The solubility of the initial and final products for reaction (1d) is, mass %:  $\text{NaCl}$  35.87<sup>20</sup> °C,  $\text{Tl}_2\text{SO}_4$  4.87<sup>20</sup> °C,  $\text{Na}_2\text{SO}_4$  21.9<sup>25</sup> °C,  $\text{TlCl}$  0.35<sup>25</sup> °C.

We have reported various aspects of modeling of the mechanism and kinetics of

TABLE 1

Physicochemical characteristics [10, 11] of the components of reaction (1a) and optimal conditions for its realization in mechanochemical reactors SPEX 8000 and AGO-2

Object, property	KBr, <i>i</i> = 1	TlCl, <i>i</i> = 2	KCl, <i>i</i> = 3	TlBr, <i>i</i> = 4	SPEX, steel	AGO, steel
<i>M</i> , g	119.01	239.85	74.55	284.31		55.85
$\rho$ , g/cm <sup>3</sup>	2.750	7.000	1.988	7.557		7.860
<i>E</i> 10 <sup>-12</sup> , dyn/cm <sup>2</sup>	0.201	0.245	0.241	0.237		2.232
<i>v</i>	0.283	0.326	0.274	0.324		0.285
$\theta \cdot 10^{12}$ , cm <sup>2</sup> /dyn	18.31	14.59	15.35	15.11		1.647
Hardness (Knupp)	6.45	12.8	8.25	11.9		~300
<i>R</i> , cm	<i>R<sub>B</sub></i> 10 <sup>4</sup> = 1.25; $\delta^* = 0.03$ ; $a^* = 0.01$				0.3	0.2
<i>N</i> *	<i>N<sub>B</sub></i> 10 <sup>-4</sup> = 6.4; <i>I</i> * = 290 cm <sup>2</sup> ; $n^* = 5 \cdot 10^6$				169	400
<i>m<sub>b</sub></i> / <i>m</i> ( <i>z</i> <sub>1</sub> <sup>*</sup> )	<i>z</i> <sub>1</sub> <sup>*</sup> = 13.5	<i>m</i> <sub>3</sub> = 0.87 g	<i>m</i> <sub>3</sub> + <i>m</i> <sub>3</sub> <sup>*</sup> = 12.66 g	9.4		6.6
<i>m<sub>b</sub></i> / <i>m</i> ( <i>z</i> <sub>2</sub> <sup>*</sup> )	<i>z</i> <sub>2</sub> <sup>*</sup> = 6.86	<i>m</i> <sub>3</sub> <sup>*</sup> = 1.52 g	<i>m</i> <sub>3</sub> + <i>m</i> <sub>3</sub> <sup>*</sup> = 11.95 g	8.5		5.9
<i>m<sub>i</sub></i> ( <i>z</i> <sub>1</sub> <sup>*</sup> ), g	1.39	2.81	11.77	3.33		<i>m</i> ( <i>z</i> <sub>1</sub> <sup>*</sup> ) = 15.97
<i>m<sub>i</sub></i> ( <i>z</i> <sub>2</sub> <sup>*</sup> ), g	2.43	4.89	10.43	5.80		<i>m</i> ( <i>z</i> <sub>2</sub> <sup>*</sup> ) = 17.75
$\lambda \cdot 10^{-4}$ , erg/(cm K s)	48.1 <sup>317</sup>	10.3 <sup>273</sup>	49.2 <sup>373</sup>	9.80 <sup>273</sup>		470
<i>c</i> 10 <sup>-6</sup> , erg/(g K)	4.52 <sup>373</sup>	2.27 <sup>373</sup>	7.03 <sup>373</sup>	1.88 <sup>293</sup>		6.60
<i>T<sub>m</sub></i> , K/°C	1003/730	703/430	1049/776	733/460		1811
<i>H<sub>m</sub></i> 10 <sup>-8</sup> , erg/g	21.85	6.504	35.29	5.768		24.7
$\mu$ , dyn s/cm <sup>2</sup>	0.0118	0.021	0.0115	0.020	–	

Note. The values of a number of important parameters obtained in the present investigation are printed in italics.

mechanochemical reactions previously [12–14], so we will use the results of those works when solving the formulated problem (Fig. 1). Let us formulate the basic postulate. At the initial period of MA of the initial powdered mixture (see equation (1)):

a) self-lining of the milling bodies with a layer of thickness *d* and porosity *p* occurs (Fig. 1, *a*, *b*);

b) homogenization is observed, that is, chemical composition is the same within a definite volume  $\Delta V = \mathbf{a} \times \mathbf{b} \times \mathbf{c}$  selected in any arbitrary point of the lined layer [15];

c) the maximal linear dimension  $\Delta V$  should be smaller than the minimal linear dimension of the volume  $\pi r^2 \delta$  [12] where *r* is the radius of the area of a shock contact of a milling body (ball) with the lined layer of particles under treatment (see Fig. 1, *a*);

d) the dynamic equilibrium is established [12, 16] with respect to the mean particle size *R<sub>i</sub>* (*i* = 1, 2, 3)  $\ll a \sim b \sim c < \delta$  with radii *R<sub>i</sub>*, distributed within one order of magnitude in layer  $\delta$  (see Figs. 1 and 2);

e) a reaction occurs (with the transformation degree  $\alpha \ll 1$ ) which results in the formation of nanoparticles of the product with the mean radii  $R_3 \approx R_4 \ll R_i$  [5–7, 17]; these particles get adsorbed or taken up by larger particles *R<sub>i</sub>* (*i* = 1, 2, 3).

The formation and evolution of the lined layer, similarly to the MA process itself, is a dynamic notion, not static one. Mass transfer within the lined layer is performed by the mobile milling bodies (ball load, see Fig. 1, *a*, *b*) during shock-friction interactions; it is accompanied by the changes in the chemical composition of the mixture, its granulometric (*R<sub>i</sub>*) and geometric ( $\delta$ ) characteristics. An  $\mathbf{a} \times \mathbf{b}$  sized fragment of an arbitrary cross section of the lined layer with similar layers imposed on it along the direction  $\langle \mathbf{c} \rangle$  is schematically shown in Fig. 2. Ideally, large particles of the reagent and diluent, their number being  $N_B = N_{1B} + N_{2B} + N_{3B}$  and radius *R<sub>B</sub>*, form the closest packing which is a superposition of the cubic and hexagonal packing. Similar particles of the mean size with radius  $R_M \approx 0.414R_B$ , their



determination of the following optimal conditions of MA: first, providing the shock-friction surface of contact between reagent particles; second, excluding aggregation of nano-sized particles of the target reaction product.

Let us establish the orders of magnitude and relations between the parameters of the problem under consideration in order to carry out specific numerical estimations. It is known [17] that the numerical value of the boundary determining a substantial difference in the physicochemical characteristics between the small particles and macroscopic bodies is  $(3 \pm 1) 10^{-6}$  cm or  $\sim 30$  nm. Therefore, the size of particles of the products of abrasive-reaction wearing of reagents is  $R_{3'} \approx R_4 \leq (3 \pm 1) 10^{-6}$  cm. On the other hand, the grinding limit in the dynamic equilibrium state was determined in [14] as the mean particle radius of  $8 \cdot 10^{-5}$  cm for NaCl and  $3 \cdot 10^{-5}$  cm for quartz ( $\text{SiO}_2$ ). Therefore, the mean value  $\langle R (i = 1, 2, 3) \rangle$  may be accepted to be approximately equal to  $5 \cdot 10^{-5}$  cm, which is quite in agreement with the condition  $R_i \gg R_{3'} \sim R_4$ . The further step is evident:  $a/2 < R_i (i = 1, 2, 3) \rangle \approx 10$ ;  $a \sim b \sim c \approx 1 \cdot 10^{-3}$  cm;  $\delta_{\min}/a \approx 10$  or  $\delta_{\min} \approx 1 \cdot 10^{-2}$  cm.

Let us also determine specific mechanochemical reactors and conditions of MA. The most important parameters to solve this problem are as follows [4-7, 10-12]: a) the ratio of mass  $m_b$  of mobile milling bodies (ball load) to the weighed portion  $m$  of the substance under treatment,  $m_b/m = 4\pi R^3 \rho N / [3(m_1 + m_2 + m_3)]$ , where  $R$ ,  $\rho$  and  $N$  are radius, density and number of balls, respectively; b) the surface area of milling bodies  $\Pi = \Pi_v + \Pi_b = \Pi_v(L_1, L_2) + 4\pi R^2 N$  where  $\Pi_v$ ,  $\Pi_b$  are the areas of the working surfaces of inner walls and ball load, respectively,  $L_1$  and  $L_2$  are radius and height of the mill cylinder, respectively. For the majority of mechanochemical reactors,  $L_1 \approx L_2 \gg R$ . Numerical estimation was made for two best known [4-7, 12-14, 18-22] mechanochemical reactors:

1. Steel ( $\rho = 7.86$  g/cm<sup>3</sup>) ball two-cylinder ( $L_1 = 3.1$  cm,  $L_2 = 4.6$  cm,  $\Pi_v = 2\pi L_1 L_2 \approx 90$  cm<sup>2</sup>, volume  $V = \pi L_1^2 L_2 \approx 140$  cm<sup>3</sup>) water-cooled planetary centrifugal mill ((the radius of planet carrier:  $L = 5.3$  cm, rotation frequency:  $\omega = 12$  s<sup>-1</sup>; opposed number of drum rotation  $\omega_1 = 29$  s<sup>-1</sup>)

AGO-2 with the following characteristics [14, 18-20]: the geometric factor  $\Gamma = L/L_1 = 1.7$ ; kinematic factor  $K = \omega_1/\omega = -2.4$ ; angle of ball detachment  $\cos \varphi = -(1 + K)/\Gamma = 0.82$ . The relative rate of milling body collisions (ball-wall and ball-ball)  $|W| = 2\pi\omega L_1[(K + 1)^2 + \Gamma^2 - 2\Gamma(K - 1)\cos \varphi + (\Gamma + 1)^2]^{0.5} \approx 1100$  cm/s, normal and tangential constituents of  $W$ :  $W_n = |W| \cos \varphi \approx 900$  cm/s и  $W_t = |W| \sin \varphi \approx 630$  cm/s.

2. A steel ball mill SPEX 8000 with the characteristics [4-7, 21, 22]:  $L_1 = 1.9$  cm,  $L_2 = 6.4$  cm,  $\Pi_v = 2\pi L_1(L_1 + L_2) \approx 100$  cm<sup>2</sup>,  $V \approx 70$  cm<sup>3</sup>,  $|\omega(\omega_k)| = 2\omega = 31$  s<sup>-1</sup>,  $W_t \approx W_n \approx 300$  cm/s.

The dynamic change in the ratio of five components proceeds during the reaction in the system ( $i = 1, 2, 3, 3', 4$ ). Let  $m_i$  and  $M_i$  be the corresponding weighed portions and molecular masses of the reagents ( $i = 1, 2$ ) and the diluent ( $i = 3$ ). The characteristics of milling bodies (without index), reagents and products of the reaction under consideration are presented in Table 1.

#### OPTIMAL PARAMETERS OF THE LINED LAYER AND MA CONDITIONS

The volume of the material under treatment  $\delta\Pi$  is obtained by the translation of a unit cell  $\Delta V = \mathbf{a} \times \mathbf{b} \times \mathbf{c}$ . Since there are no essential grounds for anisotropy of any properties of the lined layer, the choice of the shape of a cell may be arbitrary. However, taking into account the motif of the closest packing of the particles belonging to the largest mode  $N_B$ , it is reasonable to choose a cell shaped as a regular rhombohedron with edge  $|\mathbf{a}|$ , divisible by  $2R_B$ , facet area  $a^2\sqrt{3}/2$ , height  $a\sqrt{2}/\sqrt{3}$ , volume  $a^3\sqrt{2}/2$  and the length of the longer diagonal  $a\sqrt{6}$ . Taking into account that  $R_M \approx 0.414R_B$ ,  $R_S \approx 0.225R_B$  and  $2N_B = 2N_M = N_S$ , while  $\langle 2R_i (i = 1, 2, 3) \rangle \approx 1 \cdot 10^{-4}$  cm, one may easily estimate the key value  $2R_B$  on the basis of the geometric mean value  $[2R_B \cdot 2R_M(2R_S)^2]^{1/4} = 2R_B(0.41 \cdot 0.22^2)^{1/4} = \langle 2R_i (i = 1, 2, 3) \rangle \approx 1 \cdot 10^{-4}$  cm or  $2R_B \approx 2.7 \cdot 10^{-4}$  cm and on the basis of the arithmetic mean value  $2R_B(1 + 0.41 + 2 \cdot 0.22)/4 \approx 1 \cdot 10^{-4}$  cm or  $2R_B \sim 2.2 \cdot 10^{-4}$  cm. If we accept  $\langle 2R_B \rangle \approx 2.5 \cdot 10^{-4}$  cm, then  $\langle 2R_M \rangle \approx 1.0 \cdot 10^{-4}$  cm and  $\langle 2R_S \rangle \approx 0.5 \cdot 10^{-4}$  cm. Since  $\delta = \delta_{\min} = 10^{-2}$  cm =  $|\mathbf{a}_{\min}|/\sqrt{6}$ , the integer

part of the ratio  $|\mathbf{a}_{\min}|/ \langle 2R_B \rangle = 16.3$  defines the exact meaning  $|\mathbf{a}_{\min}| = 16 \langle 2R_B \rangle$ .

The maximal values  $\delta_{\max}$  and  $|\mathbf{a}_{\max}|$  may be determined on the basis of MA parameters of the lined layer. According to [10], mechanochemical reaction proceeds efficiently only within the volume  $\pi r^2 \delta$  of the shock action of milling bodies (see Fig. 1, *a*). It follows from this consideration that the longer diagonal of the rhombohedron must be shorter than the minimal linear dimension of the  $\pi r^2 \delta$  volume or  $\delta_{\max} = 2r \geq |\mathbf{a}_{\max}| \sqrt{6}$ . Otherwise not the whole volume of the unit cell will be occupied by the uniform field mechanical strain, in other words, not all the particles of the cell will be equivalent with respect to MA conditions. Since it has meanwhile been established that  $\delta \geq 10^{-2}$  cm, we may estimate the minimal diameter  $2r = 2r^*$  which corresponds to the diameter  $2r^*$  of the contact area in a collision between the lined balls (see Fig. 1, *b*, and Tables 3, 4 in [12]):

$$2r^* \text{ (lined ball + another ball of this kind)} \\ \approx 1.5R(\rho\theta)^{0.2}W_n^{0.4} \quad (2)$$

where  $\theta(z) = (km\theta_1 + hl_2\theta + z\theta_3)/(km + hl + z)$  is compliance of the material of lined layer for reaction (1). Using (2) we obtain  $\delta_{\max} = 2r^* = |\mathbf{a}_{\max}| \sqrt{6}$ ; as the optimal  $\delta = \delta^*$  value we may accept, for example, arithmetic mean  $\delta^* = (\delta_{\max} + \delta_{\min})/2 = |\mathbf{a}^*| \sqrt{6}$ . The term “optimal” means, on the one hand, that the larger size  $\delta^*$  and  $a^*$  (to be more exact, only the integer part of the  $a^*/2R_B$  ratio) may be verified physically, the easier one may correctness of the fulfilled requirement to the homogeneity of the composition of mechanically activated mixture. On the other hand, it is necessary to fulfill the condition  $m_b/m \gg 1$  [4–7]. The number  $n^*$  of optimal unit cells composing the lined layer with thickness  $\delta^*$  will be  $n^* = 2\delta^* \Pi^*/(a^*)^3 \sqrt{2} = 2\delta^* [\Pi_v + 4\pi(R^2N)]^*/(a^*)^3 \sqrt{2}$ . The use of unit cell is convenient because for any specific reaction under consideration it is invariant with respect to the type of mechanochemical reactor. In order to obtain numerical values, it is necessary to determine the optimum  $z = z^*$ .

Let us consider the structure of the lined layer or the unit cell in mode detail (see also Table 1 and Fig. 2). A cell contains  $N_B = N_{1B} + N_{2B} + N_{3B} = (a^*/\langle 2R_B \rangle)^3$  particles of the large mode  $N_B$  with radius  $R_B$  in coordination 12

forming the framework of the rhombohedron described above, the same number  $N_M$  of the particles of the medium mode with radius  $R_M$  in octahedral coordination 6 and the doubled number  $N_S$  of the small mode with radius  $R_S$  in tetrahedral coordination 4. In order to establish the distribution of particles of the reagents and diluent, or 9 unknown  $N_{iJ}$  ( $i = 1, 2, 3; J = B, M, S$ ) over three different positions of the cell, there are only three normalizing equations over the weighed portions  $m_i$ :

$$R_B^3 N_{1B} + R_M^3 N_{1M} + R_S^3 N_{1S} = 3m_1 / n^* 4\pi\rho_1 \quad (3.1)$$

$$R_B^3 N_{2B} + R_M^3 N_{2B} + R_S^3 N_{2S} \\ = 3m_1 hlM_2 / n^* 4\pi\rho_2 kmM_1 \quad (3.2)$$

$$R_B^3 N_{3B} + R_M^3 N_{3B} + R_S^3 N_{3S} \\ = 3m_1 z^* M_3 / n^* 4\pi\rho_3 kmM_1 \quad (3.3)$$

Therefore, to solve this system, it is necessary to use both the objective factors (mechanical properties of particles, for example hardness) and the subjective ones (correct prediction of the relative particle size distribution). It is reasonable to assume (see Table 1) that at the initial time of MA the hardest particles (reagent 2, TiCl) will cut more plastic ones (reagent 1, KBr; diluent 3, KCl) thus building up the basis of the cell framework, that is, occupying mainly positions B and transferring KBr and KCl particles into octahedral (O) and tetrahedral (T) cavities. It is clear that the most plastic KBr particles will occupy mainly the smallest tetrahedral cavities; therefore, octahedral cavities will be occupied mainly by the particles of medium hardness (KCl). It remains only to define more exactly what is meant by the word “mainly” from the numerical point of view. We propose the simplest and the most efficient way: while the cells free in any dimension are not filled completely, the priority of filling them is determined only by the hardness of the particles.

Let us estimate the ratio of the volume occupied by the parts of the framework of a unit cell to the total volume of particles in octahedral and tetrahedral cavities (see Fig. 2):  $R_B^3 / (R_M^3 + 2R_S^3) = 1/(0.41^3 + 2 \cdot 0.22^3) \approx 11$ . Such a substantial value will be a key in further considerations because it leads to a very important conclusion: octa- and tetrahedral

cavities of the closest packing of the lined layer on the particles under treatment may and must be occupied by only by the particles of the most plastic component! If we accept this statement as an axiom, there are two possible ways to optimize the structure of the lined layer for the reaction of general type (1):

1) the use of the hardest or not the most plastic material as a diluent: for example, let us admit the ratio of the hardness of components of mixture (1) to be similar to that of (1a), or  $B_k C_m > A_k C_l > A_h D_i$ ;

2) the hardness of diluent should be minimal ( $A_h D_i \sim B_k C_m > A_k C_l$ ); it will be hypothetically accepted in numerical estimation that in (1a) mixture the hardness of diluent (KCl) is minimal.

In the first case, an optimal value  $z = z_1^*$  can be found assuming that the most plastic reagent 1 ( $A_h D_i$ ) occupies only all the octa- and tetrahedral cavities:

$$z_1^* = \rho_3 [km\rho_2 M_1 R_B^3 - hl\rho_1 M_2 (R_M^3 + 2R_S^3)] / \rho_1 \rho_2 M_3 (R_M^3 + 2R_S^3) \quad (4a)$$

or

$z_1^* = \rho_3 [km\rho_2 M_1 - 0.0937hl\rho_1 M_2] / 0.0937\rho_1 \rho_2 M_3$  (4) since  $R_M = 0.414R_B$  and  $R_S = 0.225R_B$ . Applying (4) to reaction (1a) or accepting  $km = hl = 1$ , we obtain  $z_1^* = 13.5$ . Further we will be interested also in the ratio of the number of diluent particles  $N_{3B}$  to  $N_{2B}$  for reagent 2 (see equations (3.2) and (3.3)):  $N_{3B}/N_{2B} = \rho_3 z_1^* M_3 / (\rho_2 hl M_2)$ . For reaction (1a),  $hl = 1$  and  $N_{3B}/N_{2B} = 14.8$ . Therefore, the ratio of the number of reaction contacts of the particles of reagent 1 occupying octahedral and tetrahedral cavities to the number of simple abrasive contacts will be  $N_{2B} : N_{3B} = 1 : 14.8$ .

In the second case, the structure of the lined layer will change dramatically. All the octa- and tetrahedral cavities and a part of the cells of the closest packing will be occupied by diluent particles. The particles of reagents 1 and 2 will occupy the cells of the closest packing with radius  $R_B$  and coordination 12. Because of this, the problem is reduced to optimization of the  $N_{3B}/(N_{1B} + N_{2B}) = z'$  ratio in the cell framework. However, we are to start with the determination of the loss  $\Delta m_3$  of the weighed portion of the diluent during filling the octa-

and tetrahedral cavities:  $\Delta m_3 = n^* 4\pi\rho_3 N_B (R_M^3 + 2R_S^3) / 3$ ; the residue of the diluent  $m_3 - \Delta m_3$  will determine the number of particles  $N_{3B}$  and some other evident relations:

$$N_{3B} = z_2^* N_{1B} \rho_1 M_3 / (km\rho_3 M_1) - [N_B (R_M^3 + 2R_S^3) / R_B^3] \quad (5.1)$$

$$N_{1B}/N_{2B} = km\rho_2 M_1 / (hl\rho_1 M_2) \quad (5.2)$$

$$N_{1B} + N_{2B} + N_{3B} = N_B \quad (5.3)$$

$$N_{3B}/(N_{1B} + N_{2B}) = z' \quad (5.4)$$

where  $z = z_2^*$ , as before, determines the desired optimum of the diluent. One can see that there are only four equations for five unknowns. The following solution is obtained for this system:

$$z_2^* = \rho_3 (km\rho_2 M_1 + hl\rho_1 M_2) [z' R_B^3 + (z' + 1) \times (R_M^3 + 2R_S^3)] / (R_B^3 \rho_1 \rho_2 M_3) \quad (6)$$

or

$$z_2^* = 2.28\rho_3 (km\rho_2 M_1 + hl\rho_1 M_2) / (\rho_1 \rho_2 M_3) \quad (6a)$$

The symmetry of the closest packing and optimal MA conditions (see p. 323) dictate the choice  $z' = 2$  or  $z_2^* = 6.86$  for reaction (1a). In this case, for an arbitrarily chosen pair of contacting reagent particles the number of reaction contacts will be 3 of 12 for  $z' = 0$  [12], while the number of simple abrasive contacts will be 20 with  $N_{3B}$  particles, 12 with  $N_{3M}$  particles and 24 with  $N_{3S}$  particles.

Weighed amounts with respect to  $m_1$  for other components of reaction (1) will be:  $m_2 = m_1 hl M_2 / (km M_1)$ ,  $m_3 = m_1 z M_3 / (km M_1)$ ,  $m_{3'} = m_1 hm M_3 / (km M_1)$  and  $m_4 = m_1 lk M_4 / (km M_1)$ . Thickness  $\delta$  of the lined layer of the particles under treatment for the initial mixture of reagents (1), (2) and diluent (3) is connected with the weighed portions  $m_i$  ( $i = 1, 2, 3$ ) through the following relation [12–14]:

$$m_1 = \delta \pi \rho_3 \rho_2 \rho_1 \Pi / 4 [\rho_3 \rho_2 + \rho_3 \rho_1 hl M_2 / (km M_1) + \rho_2 \rho_1 z M_3 / (km M_1)] \quad (7)$$

Turning back to equation (2) and using the condition  $2r^*(AGO) = 2r^*(SPEX)$ , we determine such a ratio of the radii of the steel milling bodies for AGO-2 ( $R = R_{AGO}$ ) and SPEX 8000 ( $R = R_{SPEX}$ ) that will provide equal dimensions of the shock contact of milling bodies with the lined layer of particles:  $R_{AGO}/R = [W_n(SPEX)/W_n(AGO)]^{0.4} = (300/900)^{0.4} \approx 0.65$ . As a rule [18, 19],  $R_{AGO} = 0.2$  cm, therefore,  $R_{SPEX} \approx 0.3$  cm, which is also the case in experiment [7]. For reaction (1a), from equation (2) using  $\theta(z_1^*) \approx \theta(z_2^*) = 0.1554 \cdot 10^{-10}$  cm<sup>2</sup>/dyn due

to very close values of  $\theta_i$  ( $i = 1, 2, 3$ ), we obtain:  $2r^* = \delta(z_1^*) = \delta(z_2^*) = \delta_{\max} = |a_{\max}| \sqrt{6} = 4.75 \cdot 10^{-2}$  cm;  $\delta^* = (\delta_{\max} + \delta_{\min})/2 \approx 3 \cdot 10^{-2}$  cm;  $a^* = 1 \cdot 10^{-2}$  cm =  $40 \langle 2R_B \rangle$ ,  $N_B = 40^3 = 64\,000$ . In order to obtain identical geometric conditions of MA in the mills under consideration, it is also necessary to provide equal surface areas of milling bodies in them:  $(\Pi_v + \Pi_b^*)_{AGO} = (\Pi_v + \Pi_b^*)_{SPEX} = \Pi^*$  or  $N_{SPEX}^* = [(\Pi_{vAGO} - \Pi_{vSPEX}) / (4\pi R_{SPEX}^2)] + R_{AGO}^2 N_{AGO}^* / R_{SPEX}^2$ . If we accept  $N_{AGO}^* = 400$  [16, 17], then  $N_{SPEX}^* \approx 170$ , and  $\Pi^* \approx 290$  cm<sup>2</sup>. From (7) for  $km = hl = 1$  or for reaction (1a), we determine the optimal weighed portions  $m_1 + m_2 + m_3 = m(z^*)$ ,  $m_b/m(z^*)$  ratios for SPEX and AGO-2 mills, and determine the number of unit cells  $n^* = 2\delta^*\Pi^*/(a^*)^3 \sqrt{2} \approx 5 \cdot 10^6$  (see Table 1).

Now we will apply equations (4) and (6) to estimate the optimal composition of initial mixtures for reactions (1b) and (1c):  $z_1^*(1b) = 8.30$  и  $z_2^*(1b) = 4.05$ ;  $z_1^*(1c) = 17.7$  и  $z_2^*(1c) = 7.24$ . One can see that  $z^*$  values may vary within rather broad range, depending on  $\rho_i$  and  $M_i$  values of the reagents and diluents. Let us compare these values with the data determined in experiments [6, 7]:  $z_1^*(1b) = 8.2$  and  $z_2^*(1b) = 3.6$  [6];  $z^*(1c) = 12 \approx [z_1^*(1c) + z_2^*(1c)]/2$  [7]. One can see that theoretical values determined by us for the optimal parameter of powder mixture dilution  $z^*$  almost coincide with the experimental values.

So, depending on the relations between mechanical characteristics of the diluent and those of the reagents, two versions were established for the estimation of optimal ratio ( $z^*$ ) of the components in the initial powder mixtures for mechanochemical obtaining nanometer-sized particles by means of dilution with the final product. In the first case, the synthesis of the target product is carried out at 18 shock-friction contacts of quasi-spherical particles of one of the reagents comprising the closest packing together with diluent particles. The particles of another reagent occupying 6 octahedral and 12 tetrahedral cavities provide 18 mentioned contacts. The particles of the first reagent form a three-dimensional system of physical dots surrounded by the diluent particles. In the second case, the reaction proceeds between the particles of reagents only within

the framework of the closest packing separated by the diluent particles so that the contacting reagent particles form a three-dimensional network with diluent particles occupying its meshes. A substantial advantage of the described theoretical investigation is the simplicity of its application. For instance, in order to prepare a mixture of optimal composition for obtaining nanometer-sized product of mechanochemical synthesis according to reaction (1), it is necessary for processing engineers to calculate only the value of dilution parameter  $z^*$  using the simplest and more accurate equations (4a) or (6a) on the basis of the relations between the hardness characteristics of reagents and the diluent. In order to choose the necessary equation and carry out calculation according to (4a) or (6a), we use only the best-known technological parameters: molecular mass  $M_i$ , density  $\rho$  and hardness  $H_i$  of the components of the mixture. As a rule, these components are well-studied chemical elements or individual chemical compounds.

#### ESTIMATION OF THE KINETICS OF ABRASIVE-REACTION WEARING OF REAGENTS

In the previous sections, for theoretical consideration of mechanochemical reactions as example, we estimated the optimal value of dilution parameter  $z$  for obtaining nanometer-sized particles like TlBr and a number of other compounds according to exchange reactions like (1). In the considered reactions, the hardness of the substances under treatment is much below the hardness of the steel milling bodies. Because of this, we may neglect abrasive-reaction wearing of the material of milling bodies studied in [14, 18, 19, 23] and shown schematically in Fig. 1, a, b. The mechanisms and kinetics of the traditional mechanochemical reactions were investigated in [12, 13, 24, 25]. In this section, we consider only specific features of the application of the results of these works to estimations of the kinetics of abrasive-reaction nano-wearing of the particles of substances under treatment due to the following differences:

- 1) addition of one of the reaction products (a diluent) to the initial reagent mixture;



2) the relations between mechanical characteristics of the diluent and those of reagents, for example, the ratio of diluent hardness and reagents hardness;

3) the occurrence of a three-modal size distribution of the particles under treatment.

A model for the estimation of the characteristics of shock-friction interaction of two contacting reagent particles chosen arbitrarily from the region  $\pi r^2 \delta$  of the shock action of milling bodies upon the lined layer of particles is shown in Fig. 1, c; the key parameters to calculate a rate of any mechanochemical reaction are shown in Fig. 1, d. Below we will consider the case admitting the most general mathematical description of the interaction between milling bodies: a collision of a non-lined ball with the lined wall of the cylinder of AGO-2 mill (see Fig. 1, a). A dummy degree  $\alpha_f$  of mechanochemical transformation according to reaction (1) is described by equations [12, 13]

$$\alpha_f(\tau) = \Psi(z)\Phi^*n(\tau)[V^*(\tau)/V(\tau)] \quad (8)$$

$$V^*(\tau) = \sum_1^n V^*(n) = \sum_1^n g(z)d^*(n)s_{1,2}(n) \quad (8a)$$

$$V(\tau) = V(0) - \sum_1^n V^*(\tau) \quad (8b)$$

$$n(\tau) = \zeta\eta\psi\omega_1 \quad \tau = f\tau \quad (8c)$$

$$\psi = 2^{-4}[10\pi\rho(\theta + \vartheta)W_n^2]^{0.4} \\ = 0.25[\rho(\theta + \vartheta)W_n^2]^{0.4} \quad (8d)$$

Here (see also Table 1 and Fig. 1, d)  $\Psi(z)$  is a dimensionless function of dilution parameter  $z$  taking into account mass transfer in the lined layer for the generation of new contacts between reagent particles;  $\tau \geq \tau'$  is a current MA time after the formation of lined layers on the surface of milling bodies and the achievement of quasi-equilibrium state with respect to particle dimensions;  $V(0; \tau = \tau')$  is total volume of particles 1 and 2;  $\Phi^*$  is the fraction of reacted material within volume  $V^*$ ;  $V^*(n)$  is the reaction volume, or a decrease in the volume  $V = V_1 + V_2$  of a pair of particles as a result of their single (number  $n$ ) abrasive-reaction interaction;  $g(z)$  is the number of identical abrasive-reaction contacts of a selected pair of particles (see Fig. 1, d) taking into account dilution parameter  $z$ ;  $d^*(n)$  and  $s_{1,2}(n)$

are the thickness of reaction zone and the area of shock-friction contact between a pair of particles 1 and 2, respectively;  $n(\tau)$  and  $f$  are the number and frequency of shock-friction interactions between the two selected particles, respectively;  $\zeta$  is the coefficient of collective action of the ball load, which is approximately equal to  $N$ ;  $\eta \sim N(R/L_1)^2$  is a parameter taking into account the geometric characteristics of MA (as a rule [12], for rather large number of balls  $N = 400$  for AGO-2 mill,  $\zeta\eta \approx 1$ );  $\psi$  is the geometric probability for an arbitrarily chosen pair of particles to get into volume  $\pi r^2 \delta$ .

There is the following correlation between the real ( $\alpha$ ) and dummy ( $\alpha_f$ ) degrees of transformation according to reaction [12]  $d\alpha(\tau) = (1 - \alpha)^p d\alpha_f(\tau)$ , where  $p$  is a parameter taking into account the effect of the final products on the reaction kinetics. In application to reaction (1), we may accept  $p = 1$  (it is known [24] that the linear law of the effect of the formed final products provides the most adequate description of the available experimental kinetic regularities of mechanochemical reactions). Therefore,

$$-\ln[1 - \alpha(\tau)] = \alpha_f(\tau). \text{ Let us estimate } \sum_1^n V^*(n).$$

If  $\xi(1) = V^*(1)/V(0) = 3g(z)d^*(1)s_{1,2}(1)/[4\pi(R_1^3 + R_2^3)]$  describes the fraction of eliminated volume at the contacts of a chosen pair of particles during their first interaction, then, we obtain for consecutive interactions:  $\xi(n) = V^*(n)/[V(n - 1)]$ . It was confirmed in [13] that  $\xi = \xi(1) = \xi(2) = \dots = \xi(n)$ . The constancy of  $V^*(n)/[V(n - 1)]$  value for any  $n = f\tau$  allows us to write down:

$$\sum_1^n V^*(n) = \xi V(0)[1 + (1 - \xi) + (1 - \xi)^2 + \dots \\ + (1 - \xi)^n] = V(0)[1 - (1 - \xi)^n] \quad (9)$$

$$V^*(\tau)/V(\tau) = [1 - (1 - \xi)^n]/(1 - \xi)^n \quad (9a)$$

The final equations for the degree  $\alpha(\tau, z)$  of transformation according to reactions like (1) will be:

$$-\ln[1 - \alpha(\tau, z)] = \alpha_f(\tau, z) \\ = \Psi(z)\Phi^*f\tau[1 - (1 - \xi)^{f\tau}]/(1 - \xi)^{f\tau} \quad (10)$$

$$\xi(z) = V^*(1)/V(0) \\ = 3g(z)d^*(1)s_{1,2}(1)/[4\pi(R_1^3 + R_2^3)] \quad (10a)$$

Numerical estimation of the parameters of the resulting kinetic equation (10) will be carried out with respect to reaction (1a) taking into

account the fact that the mechanism of this mechanochemical reaction is due to the contact melting of particles [9, 24, 25].

It follows from equations (8c) and (8d) for  $\theta + \vartheta = 0.172 \cdot 10^{-10} \text{ cm}^2/\text{dyn}$  and  $\zeta(N=400)\eta(N=400) \approx 1$  [12] that  $n(\tau) = \zeta\eta\psi\omega_1\tau = 0.25[\rho(\theta + \vartheta)W_n^2]^{0.4}\zeta\eta\omega_1\tau = f\tau$  и  $f = 0.189 \text{ s}^{-1}$ , that is, the shock-friction interaction of any contacting particles in AGO-2 mill takes part every 5 s. We have already determined the parameters  $g(z = z^*)$  of abrasive-reaction contacts between the particles of reagents 1 and 2:  $g(z_1^*) = 18$  is the number of contacts of the particles of reagent 2 ( $R_2 = R_B$ ) with the particles of reagent 1 occupying 6 octahedral ( $R_1 = R_M$ ) and 12 tetrahedral ( $R_1 = R_S$ ) cavities adjacent to  $R_2$  particles;  $g(z_2^*) = 3$  is the number of contacts in the chains of alternating particles of reagents 1 and 2 in the framework of the closest packing ( $R_1 = R_2 = R_B$ ). We have already mentioned that exchange reactions like (1) proceed only on abrasive-reaction contacts between the particles of reagents 1 and 2, while substantially larger number of abrasive contacts of reagents with the particles of diluent 3 does not lead to the reaction. Because of this, the role of function  $\Psi(z)$  is to take into account mass transfer by milling bodies for the generation of new contacts between reagent particles in order to achieve completion of the exchange reaction. It is evident that the organization of new contacts by means of mass transfer is connected with dilution degree  $z$ , the structure of the lined layer (see Fig. 2) and requires some addition MA time, that is,  $\Psi(z) < 1$ . In our opinion, the following equations meet these requirements:

$$\Psi(z_1^*) = N_{2B}(z_1^*)/N_{3B}(z_1^*) = 1/14.8 = 0.0675 \quad (11a)$$

$$(z_2^*) = g(z_2^*)/g(R_{2B}, R_{1B} \rightarrow R_{3B}, R_{3M}, R_{3S}) = 3/(20 + 12 + 24) = 0.0536 \quad (11b)$$

Since the mechanism of reactions (1a) and (1d) under investigation in the present work is due to the contact melting of particles 1 and 2 occurring at a temperature  $T_{c,m} \leq T_{m2}$  (not higher than the melting point  $T_{m2}$  of the most easily melting reagent 2, see Table 1), function  $\Phi^*$  can be calculated [24]. So, in equations (10), it remains only to determine the numerical value

of the key parameter  $\xi$  and to find the time of MA  $\tau$  corresponding to the transformation degree of the selected model reaction (1a) 99 %, for example, from the condition  $\alpha(\tau = \tau^*) = 0.99$ .

Equation for the area of abrasive-reaction contact  $s_{1,2}(1)$  in (10a) is known [12]:

$$s_{1,2}(1, z) = 3.1 R_{1,2}^2 \rho^{0.4} (\theta + \vartheta)^{-1.6} (\theta_1 + \theta_2)^2 W_n^{0.8} \quad (12)$$

where  $R_{1,2}(z) = R_1 R_2 / (R_1 + R_2)$ . Let us consider a general case when  $z = z_1^*$ . Reactions of the particles of reagents 1 and 2 proceed at the contacts of the particles of reagent 1 having  $R_1 = R_M$  and  $R_1 = R_S$  with the particles of reagent 2 having  $R_2 = R_B$ . In reality, an ideal structure of the lined layer (see Fig. 2) is unachievable. Because of this, both to simplify calculations and to provide their more real description, it is reasonable to accept the mean size of octahedral and tetrahedral cavities:  $\langle R_M, R_S \rangle = R_{MS} = (6R_M + 12R_S)/18 = 0.333 \cdot 10^{-4} \text{ cm}$  and  $R_{12}(z_1^*) = R_{MS} R_B / (R_{MS} + R_B) = 0.263 \cdot 10^{-4} \text{ cm}$ . For  $z = z_2^*$ :  $R_1 = R_2 = R_B$  и  $R_{12}(z_2^*) = R_B/2 = 0.625 \cdot 10^{-4} \text{ cm}$ . Calculation according to (12) for  $\theta_1 + \theta_2 = 0.329 \cdot 10^{-10} \text{ cm}^2/\text{dyn}$  gives:  $s_{1,2}(z_1^*) = 2.07 \cdot 10^{-10} \text{ cm}^2$  and  $s_{1,2}(z_2^*) = 11.7 \cdot 10^{-10} \text{ cm}^2$ .

When we calculate  $d^*(1, z) = 2d_{1,2}(z)$  where  $d_{1,2}$  is the thickness of contact melting zone of particles 1 and 2 from the initial surface of relative shift (viscous flow [25]) during their shock-friction interaction (see Fig. 1, c, d) we also use values [12]:  $\rho_{1,2}(z_1^*) = \rho_1 \rho_2 (R_{MS} + R_B)^3 / (\rho_1 R_{MS}^3 + \rho_2 R_B^3) = 5.55 \text{ g/cm}^3$  and  $\rho_{1,2}(z_2^*) = 8\rho_1 \rho_2 / (\rho_1 + \rho_2) = 15.8 \text{ g/cm}^3$ ;  $\rho_i R_j^2(z_1^*) = \rho_1 \rho_2 R_{MS}^2 R_B^2 (R_{MS} + R_B) / (\rho_1 R_{MS}^3 + \rho_2 R_B^3) = 0.384 \cdot 10^{-8}$  and  $\rho_i R_j^2(z_2^*) = 2\rho_1 \rho_2 R_B^2 / (\rho_1 + \rho_2) = 6.17 \cdot 10^{-8} \text{ g/cm}$ ;  $B = \xi_{1,2} W_n (\rho/\rho_{1,2})^{0.5} (\theta + \vartheta)^{-2} \times (\theta_1 + \theta_2) (\rho_1 \rho_2 c_1 c_2 \lambda_1 \lambda_2)^{-0.25}$ ,  $B(z_1^*) = 539 \cdot 10^5$  and  $B(z_2^*) = 319 \cdot 10^5 \text{ K/s}^{0.5}$  where  $\xi_{1,2}$  is the coefficient of dynamic friction, equal to 0.8;  $\langle \rho \rangle = (\rho_1 + \rho_2)/2 = 4.875 \text{ g/cm}^3$ ,  $\langle c \rangle = (c_1 + c_2)/2 = 3.4 \cdot 10^6 \text{ erg/(g K)}$ ,  $\langle H_m \rangle = (H_{m1} + H_{m2})/2 = 14.18 \cdot 10^8 \text{ erg/g}$ ;  $\langle \mu \rangle = (\mu_1 \mu_2)^{0.5} = 0.016 \text{ dyn s/cm}^2$ ;  $T_{c,m} \approx T_{m2}$ ,  $T_{m2} - T_0 \approx \Delta T_m = 350 \text{ K}$  [12–14] (see Table 1).

A detailed deduction of equations for the calculation of the parameters of melting zone was described in [24–26]:

$$d^*(z) = 2w_t(z)[f(y, h)(\tau'_m - \tau_m)\langle \mu \rangle / \langle c \rangle (\langle H_m \rangle + \langle c \rangle \Delta T_m)]^{0.5} \quad (13)$$

Here  $w_t(z) = 0.57\rho^{0.3}\rho_{1,2}^{-0.5}(\theta + \vartheta)^{-1.2}(\theta_1 + \theta_2)W^{0.6}$  is the relative velocity of the viscous shift of particles 1 and 2,  $w_t(z_1^*) \approx 7200$ ,  $w_t(z_2^*) \approx 4300 \text{ cm/s}$ ; the time of melt existence on the

contacts between particles  $\tau'_m - \tau_m \approx 100 \cdot 10^{-10}$  s for  $z = z_1^*$ ,  $\tau'_m - \tau_m \approx 570 \cdot 10^{-10}$  s for  $z = z_2^*$ ;  $\tau_m = (\Delta T_m / B \cdot \text{iErfc}[0])^2 = (626/B)^2$ , where  $\text{iErfc}[*]$  is a tabulated function of the error integral and  $\text{iErfc}[0] = 0.5642$ ;  $\tau'_m = (\tau_{1,2} + \tau_m)^2 / (4\tau_m)$ ;  $\tau_{1,2} = 3.5\rho^{-0.1}(\rho_i R_j^2)^{0.5}(\theta + \Theta)^{0.4}W^{-0.2}$  is the time of shock-friction interaction between particles 1 and 2,  $\tau_{1,2}(z_1^*) = 22 \cdot 10^{-10}$  s,  $\tau_{1,2}(z_2^*) \approx 90 \cdot 10^{-10}$  s; parameter  $y = (\tau'_m / \tau_m) - 1$ ,  $y(z_1^*) \approx 77$ ,  $y(z_2^*) \approx 150$ ;  $h = \pi^{0.5} \langle c \rangle \Delta T_m / \langle H_m \rangle \approx 1.5$ ;  $f(y, h)$  is a tabulated function in the theory of contact melting [26],  $f(75, 1.5) \approx f(150, 1.5) \approx 0.9$ . Calculation according to (13) gives:  $d^*(z_1^*) \approx 1.6 \cdot 10^{-6}$  cm и  $d^*(z_2^*) \approx 2.2 \cdot 10^{-6}$  cm.

The high-rate ( $\sim 10^5$  K/s) quenching – crystallization of the melt – causes the formation of the final reaction products; the size of the new formed phases cannot exceed  $d^*$  [24]. That is why abrasive-reaction wearing of the contacting reagent particles 1 and 2 always leads to the formation of nanometer-sized product particles as a result of a reaction of the type of (1); the presence of diluent 3 provides conservation of the dimensions of the target product 4. Now let us assume that the mechanism of reaction (1a) in AGO-2 mill is identical to the mechanism of reaction  $\text{KCl} + \text{NaNO}_3 = \text{KNO}_3 + \text{NaCl}$  in a similar mill EI 2x150 [9, 24]. The rate of this reaction is limited by the depth of mutual diffusion of reagents in the melted zone. The degree of transformation for this reaction within volume  $V^*$  is determined to be  $\Phi^* \approx 0.65$  [24]. Accepting the same  $\Phi^*$  value for reaction (1a) we may calculate kinetic curves  $\xi(\tau, z^*)$  according to (10) and the values of  $\xi(z^*)$  according to (10a); as a consequence, for  $\alpha(\tau, z^*) = 0.99$  the time of MA  $\tau = \tau^*(z^*)$  for the model reaction (1a) to proceed by 99 %:

$$\begin{aligned} \xi(z_1^*) &= 3g(z_1^*)d^*(z_1^*)s_{1,2}(z_1^*)/[4\pi(R_{MS}^3 + R_B^3)] \\ &= 0.000697 \end{aligned} \quad (141)$$

$$\begin{aligned} \xi(z_2^*) &= 3g(z_2^*)d^*(z_2^*)s_{1,2}(z_2^*)/(8\pi R_B^3) \\ &= 0.000155 \end{aligned} \quad (142)$$

$$-\ln[1 - \alpha(\tau, z^*)] = \Psi(z^*)\Phi^*f\tau^*[1 - (1 - \xi)^{f\tau^*}] / (1 - \xi)^{f\tau^*} \quad (15)$$

$$\Psi(z^*)\Phi^*f\tau^*[1 - (1 - \xi)^{f\tau^*}] = 4.60(1 - \xi)^{f\tau^*} \quad (15a)$$

The dependencies of transformation degree  $\alpha(\tau, z^*)$  for reaction (1a) on the number  $f\tau$  of abrasive-reaction contacts and MA time  $\tau$  in AGO-2 planetary mill calculated according to equation (15) are shown in Fig. 3. Using equations

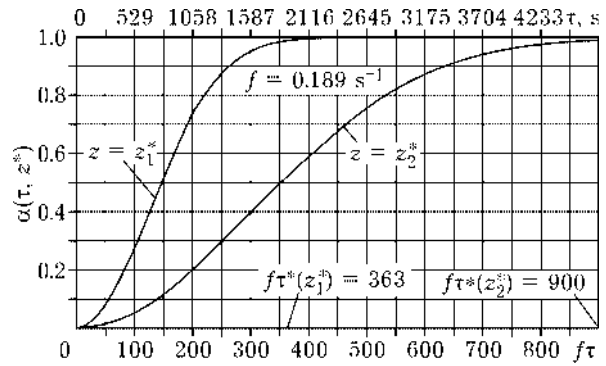


Fig. 3. Kinetic curves  $\alpha(\tau, z^*)$  for reaction (1a) in AGO-2 mill, calculated according to equation (15).

(11) and (14) we obtain the following solutions of equation (15a) for the time  $\tau^*$  of reaction (1a) to proceed by 99 % after establishment of the mechanochemical quasi-equilibrium with respect to the size of mechanically activated particles in AGO-2 mill for  $f = 0.189 \text{ s}^{-1}$ :  $f\tau^*(z_1^*) \approx 363$  and  $\tau^*(z_1^*) \approx 1900 \text{ s} \approx 32 \text{ min}$ ;  $f\tau^*(z_2^*) \approx 900$  and  $\tau^*(z_2^*) \approx 4800 \text{ s} \approx 80 \text{ min}$ . In experiments described in [6, 7], the kinetics of reactions (1b) and (1c) was not investigated; however, the chosen time of MA  $\tau = 120 \text{ min}$  turned out to be sufficient for their completion. Theoretical values of  $\tau^*$  determined by us do not exceed 2 h and not only agree but also supplement the experimental values by the new data in the aspect of kinetic regularities.

#### EXPERIMENTAL VERIFICATION OF MODELING RESULTS

The detailed conditions for the performance of the reference exchange reaction (1d) in a steel water-cooled two-cylinder ball mill AGO-2 are shown in Table 2 ( $m_3$  is the mass of diluent  $\text{Na}_2\text{SO}_4$  additionally formed in the reaction). Judging from the hardness of reagents ( $\text{NaCl}$ , halite,  $i = 1$ ;  $\text{Tl}_2\text{SO}_4$ , thallium sulphate,  $i = 2$ ) and the diluent ( $\text{Na}_2\text{SO}_4$ , thenardite,  $i = 3$ ), the conditions of optimal dilution for reaction (1d) should be described according to (4) by the parameter  $z_1^* = 11.25$  because, as a rule, the hardness of sulphates [27, 28] is higher than that of halides. Nevertheless, since we did not succeed in finding the hardness of  $\text{Tl}_2\text{SO}_4$  crystals in literature, and in order to verify the results obtained with the help of the theory, we chose both compositions for the experiments

TABLE 2

The characteristics of components and optimal experimental conditions to conduct reaction (1d)

Characteristics	NaCl, <i>i</i> = 1	Tl <sub>2</sub> SO <sub>4</sub> , <i>i</i> = 2	Na <sub>2</sub> SO <sub>4</sub> , <i>i</i> = 3	TlCl, <i>i</i> = 4	AGO-2, steel <i>R</i> = 0.2 cm	<i>N</i> = 401
Hardness (Moos) [27, 28]	2–2.5	–	2.5–3	–	<i>R<sub>B</sub> : R<sub>M</sub> : R<sub>S</sub> =</i>	4–5
Hardness (Knupp) [10]	(15.2)	(–)	(–)	(12.8)	<i>5 : 2 : 1;</i>	(~300)
<i>M</i> , g	58.44	504.80	142.04	239.85	<i>m<sub>b</sub> = 97.1 g;</i>	
<i>ρ</i> , g/cm <sup>3</sup>	2.165	6.675	2.663	7.000	<i>τ* = 6300 s;</i>	7.86
<i>m<sub>i</sub>(z<sub>1</sub><sup>*</sup>)</i> , g	1.106	4.832	14.97	4.491	<i>m(z<sub>1</sub><sup>*</sup>) = 20.77;</i>	
<i>m<sub>i</sub>(z<sub>2</sub><sup>*</sup>)</i> , g	1.900	8.206	12.5747.798		<i>m(z<sub>2</sub><sup>*</sup>) = 22.68 ;</i>	
<i>m<sub>b</sub>/m(z<sub>1</sub><sup>*</sup>)</i>	<i>z<sub>1</sub><sup>*</sup> = 11.25</i>	<i>f = 0.189 s<sup>-1</sup></i>	<i>m<sub>3</sub> + m<sub>3</sub>' = 16.300 g</i>		<i>Ψ(z<sub>1</sub><sup>*</sup>, τ*) = 0.0046</i>	4.68
<i>m<sub>b</sub>/m(z<sub>2</sub><sup>*</sup>)</i>	<i>z<sub>2</sub><sup>*</sup> = 5.44</i>		<i>m<sub>3</sub> + m<sub>3</sub>' = 14.883 g</i>			4.28

Note. The values of some necessary parameters are printed in italics.

\* Optimal conditions.

(see Table 2 and equations (4), (6)). The mixtures of reagents of “kh.ch.” and “ch.” (Tl<sub>2</sub>SO<sub>4</sub>) grades corresponding to stoichiometric compositions with  $z = z_1^*$  and  $z = z_2^* = 5.44$  were preliminarily ground and homogenized for 1 h in Fritsch Pulverizette mill with steel equipment (a mortar 9.45 cm in diameter and one ball 5.16 cm in diameter). The initial mean particle size for thus obtained mixtures was determined from the data of optical microscopy to be equal to 0.005–0.015 cm, that is, the size was far from the dimensions in the quasi-equilibrium state during MA:  $\langle R_i \rangle \approx 1 \cdot 10^{-4}$  cm. The products of MA were investigated by means of the standard powder X-ray phase analysis (XPA) [9, 29–34] with DRON-3 diffractometer. The filtered CuK<sub>α</sub> radiation was used with the 2θ angle scanning rate of 1°/60 s, as a rule.

The kinetics of reaction (1d) was investigated by measuring the conductivity of aqueous solutions of samples (1 g per 10 ml of deionized water) of the resulting products. The only poorly soluble product in the system under investigation is TlCl, which ensured rather high accuracy of measurements of a decrease in the conductivity of mechanically activated product samples in comparison with the samples of initial homogenized samples. This method was well approved by us for the separate determination of isomers: ammonium thiocyanate (NH<sub>4</sub>CNS pseudo-halide) and thiocarbamide (molecular non-conducting crystal, (NH<sub>2</sub>)<sub>2</sub>CS) present together in solutions [35, 36].

A set-up for conductivity measurements was constructed on the basis of Impedance Meter BM507 (Tesla, Brno) and Pt electrode (Conductometric Bell Electrode, type OK-9023, Radelkis Electrochemical Instrument, Budapest). Measurement error was determined from the following characteristics of the system. Maximal possible TlCl content in the sample (with a mass of 1 g) is  $4.491/20.77 \approx 0.216$  g, Tl<sub>2</sub>SO<sub>4</sub>  $8.206/20.77 \approx 0.395$  g. About 3.5 mg of TlCl and 48.7 mg of Tl<sub>2</sub>SO<sub>4</sub> can be dissolved in 1 ml of water. Let us accept the solubility of mechanically activated TlCl particles to be about 10 times smaller than the solubility of Tl<sub>2</sub>SO<sub>4</sub> particles, that is, about 5 mg of TlCl can be dissolved in 1 ml of water (it is known from [37] that the solubility of mechanically activated salts can exceed their tabulated equilibrium solubility). Therefore, for the sample mass of 1 g, about 50 mg of TlCl and certainly all the other components of the system will be dissolved in 10 ml of water; so,

– the error of conductivity measurement only on the basis of electric conductance of the solutions of MA samples would be  $0.05/0.216 \approx 23$  %;

– calibration (record of the conductivity curve with the initial reagent mixtures of different compositions) allows us to reduce the measurement error to  $(0.05–0.035)/0.216 \approx 7$  %;

– the introduction of correction coefficient 2 (averaging over the composition or at the half of transformation degree of the reaction under investigation) allows us to increase the accuracy of measurements to ~4 %;

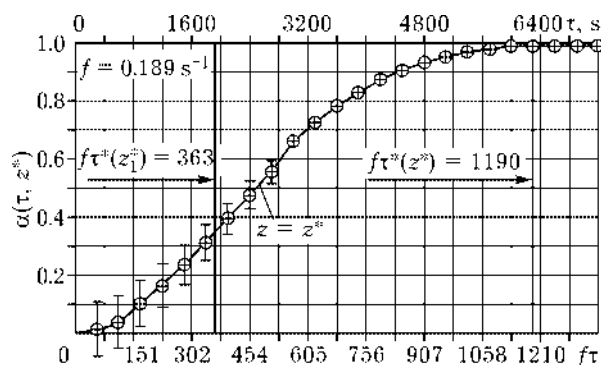


Fig. 4. Experimental curve  $\alpha(\tau, z^*)$  for reaction (1d) plotted on the basis of conductivity measurements in the solutions of mechanically activated samples.

– the diameter of experimental dots on the kinetic curve (Fig. 4) of the course of reaction (1d) corresponds to this latter measurement error.

The data of XPA were used also for rough monitoring of the results obtained (the dynamics [29] of the process or the transformation degree [9] were characterized on the basis of relative changes in the main diffraction peaks of crystal phases).

When investigating the kinetics of reaction (1d) we came across some difficulties. It was expected that the time of MA for the completeness of reaction (1d) should be approximately equal to the calculated  $\tau^*(z^*)$  values (see Fig. 3):  $\tau^*(z_1^*) \approx 1900$  s and  $\tau^*(z_2^*) \approx 4800$  s. We chose deliberately longer MA time 7200 s for preliminary experiments. However, it turned out (see Fig. 4) that the reaction proceeded till completeness ( $\alpha \approx 1$ ) only in the sample with  $z = z_1^*$ , while for the sample with  $z = z_2^*$  the transformation degree did not exceed  $\sim 0.4$ . The result of XPA of a sample for  $z = z_1^*$  which is a superposition of reflections of the initial reagents (NaCl, see, for example, PDF 77-2064, and  $\text{Ti}_2\text{SO}_4$ , PDF 7-188) and the diluent ( $\text{Na}_2\text{SO}_4$ , PDF 74-2036) is shown in Fig. 5. However, it should be noted that as early as during homogenization (see Fig. 5, a) for  $2\theta \approx 33^\circ$  a reflection of the reaction product may be detected:  $\text{TiCl}$ , PDF 6-486. The result of MA of the sample with  $z = z_1^*$  is shown in Fig. 5, b. One can see that reaction (1d) is complete. Because of this, we carried out further investigations with the samples characterized by  $z = z_1^* = z^*$  (see Fig. 4). The data obtained are likely to confirm our assumption concerning the ratio of reagents hardness of the initial

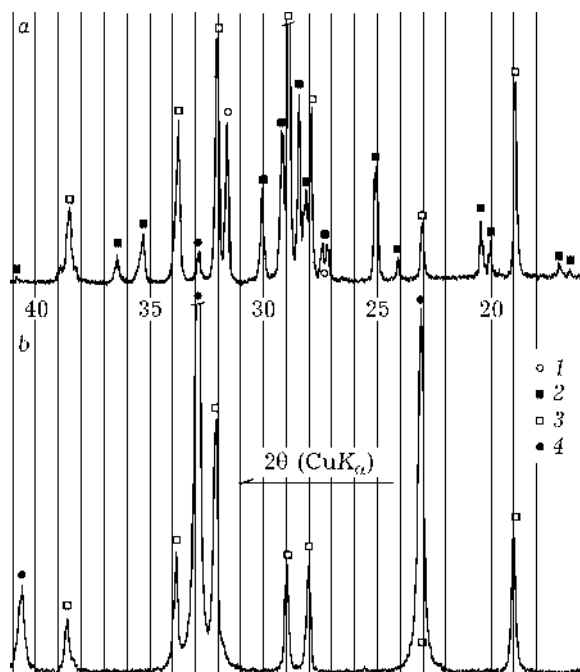


Fig. 5. XPA data of samples: a – the initial mixture of reagents for reaction (1d) with  $z = 11.25$ , homogenized for 1 h in Fritsch Pulverizette-7 mill; b – homogenized mixture subjected to MA in AGO-2 mill for 7200 s: 1 – NaCl, 2 –  $\text{Ti}_2\text{SO}_4$ , 3 –  $\text{Na}_2\text{SO}_4$ , 4 –  $\text{TiCl}$ .

mixture for reaction (1d). A similar relation was obtained in theoretical calculation of the mechanism and kinetics of the model reaction (1a) for  $z = z_1^*$ .

It was assumed that the experimental kinetic curves would be obtained using only two samples with  $z = z_1^* = z^*$  (AGO-2 mill, cooled with water, which is of principal importance for achievement of some specific results [38], operating with two cylinders [18, 19]). Sampling was carried out in turn from each cylinder after each 300 s interrupting MA (total time of MA interruption did not exceed 1500 s) in the amount of  $\sim 0.3$  g, which is very small in comparison with the weighed portion of mechanically activated samples ( $\sim 20$  g) and was expected not to affect the course of reaction (1d). However, the results of comparison of transformation degree, for example for a sample activated mechanically for 1800 s as a total ( $\alpha \approx 0.15$ ) with that for a sample activated for the same time without interruption ( $\alpha \approx 0.3$ ) demonstrated the crucial effect of MA interruption [4, 39] on the reaction kinetics. Because of this, further we investigated the

reaction kinetics (1 g) in the continuous regime of MA.

**DISCUSSION OF RESULTS**

Equations (14), (15) for the description of kinetic parameters (16), (17) and the kinetic curve (18) for the course of model reaction (1a) in AGO-2 mill will be written down as follows:

$$\Psi(z_1^*) = N_{2B}(z_1^*)/N_{3B}(z_1^*) = 1/14.8 = 0.0675 \quad (16)$$

$$\xi(z_1^*) = 3g(z_1^*)d^*(z_1^*)s_{1,2}(z_1^*)/[4\pi(R_{MS}^3 + R_B^3)] = 0.000697 \quad (17)$$

$$-\log [1 - \alpha(\tau, z_1^*)] = \Psi(z_1^*)\Phi^*f\tau \times [1 - (1 - \xi)^{f\tau}]/(1 - \xi)^{f\tau} \quad (18)$$

$$f\tau^*(z_1^*)[1 - (1 - \xi)^{f\tau^*(z_1^*)}]/(1 - \xi)^{f\tau^*(z_1^*)} = 4.60/\Psi(z_1^*)\Phi^* \approx 105 \quad (19)$$

It follows from  $\alpha(\tau = \tau^*, z_1^*) = 0.99$  that  $-\ln [1 - \alpha(\tau^*, z_1^*)] = 4.60$  and (19). In these equations, the only term insufficiently substantiated theoretically or anyway experimentally is  $\Psi(z)$ , a dimensionless function of dilution parameter  $z$  taking into account mass transfer of the material under treatment on the mobile milling bodies in the lined layers for the generation of new contacts between reagent particles. Up to present, we are unaware of any works investigating mass transfer in mechanochemical reactors. It is evident that with the experimentally available kinetic curve the numerical value of function  $\Psi(z^*)$  can be determined from (18) for any specific  $\alpha = \alpha'$ . Moreover, unlike for the theory, temporal dependence of this function  $\Psi(z^*, \tau)$  can also be established.

Let us admit (see (17)) that  $\xi(z_1^*) \approx \xi(z^*)$ , where the dimensionless parameter  $\xi(z^*)$  describes the fraction of eliminated volume  $V^*/V$  at the shock-friction contact of a selected pair of particles with total volume  $V$  for the reaction under investigation (1d). The difference in  $\xi(z_1^*)$  and  $\xi(z^*)$  values is due only to the differences

in density  $\rho$  and compliance  $\theta = 4(1 - \nu^2)/E$  of reagents in reactions (1a) and (1d), where  $E$  and  $\nu$  are Poisson coefficient and Young's modulus, respectively. Only  $\rho$  and  $\theta$  differ when we calculate  $d^*(z_1^*)$  and  $s_{1,2}(z_1^*)$  – the thickness of reaction volume  $V^*$  and the area of shock-friction contact of a selected pair of particles, respectively; so,  $V^* = d^*(z^*)s_{1,2}(z^*)$ .

This allows us (see Fig. 4) for the first time to carry out experimental estimation of mass transfer coefficient  $\Psi(z^*)$  during MA. Indeed, conductometric measurements show that the reaction is completed after MA for approximately  $\tau = \tau^* = 6300$  s; further MA has not effect on the results of measurements. Let us accept time of MA  $\tau^*$  as a marker of the (1d) reaction progress by 99 %. Then, the following equations and estimation of the  $\Psi(z^*, \tau)$  function are consequences of (16) and (17):

$$\Psi(z^*, \tau^*) \approx 7.1(1 - \xi)^{f\tau^*(z^*)}/f\tau^*(z^*)[1 - (1 - \xi)^{f\tau^*(z^*)}] = 0.0046 \quad (20)$$

$$\Psi(\tau) = -\ln [1 - \alpha(\tau)] \times (1 - \xi)^{f\tau} / \{\Phi^*f\tau[1 - (1 - \xi)^{f\tau}]\} \quad (21)$$

It follows from (20) that at the final stage of reaction (1d)  $\Psi(z^*, \tau^*) \approx 0.0046$ .

Equation (21) for  $\Psi(\tau)$  is evidently non-linear, so it seems reasonable to continue investigation of the properties of function  $\Psi(\tau)$ . The calculated  $\Psi(\tau)$  values within  $1 - \alpha(\tau)$  variation interval from 0.9 to 0.07 are presented in Table 3. Even a fleeting glance at the results obtained is sufficient to establish the trigonometric (most probably damped and shrinking sinusoid) character of function  $\Psi(\tau)$ .

An explanation of such a regularity of  $\Psi(\tau)$  changes seems not very complicated. At the beginning of MA of the mixture (within the first 10 min) the prevailing process is self-lining of milling bodies, so the mean mass transfer coefficient at this stage of MA  $\langle \Psi(\tau = 300 \text{ s}) = 0.0065 \approx \Psi(\tau = 600 \text{ s}) = 0.0058 \rangle \approx 0.0061$  is less

TABLE 3  
Calculated changes in parameters  $f\tau$ ,  $\alpha(\tau)$  and  $\Psi(\tau)$  depending on MA time  $\tau$

Parameter	$\tau$ , s										
	900	1200	1500	2100	2400	2700	3000	3300	3900	4200	4800
$f\tau$	170	227	283	397	454	510	567	624	737	794	907
$\alpha(\tau)$	0.10	0.16	0.23	0.39	0.47	0.55	0.66	0.72	0.83	0.87	0.93
$\Psi(\tau) \cdot 10^3$	7.6	6.9	6.5	6.0	5.8	5.6	6.0	0.45	0.55	5.4	5.1

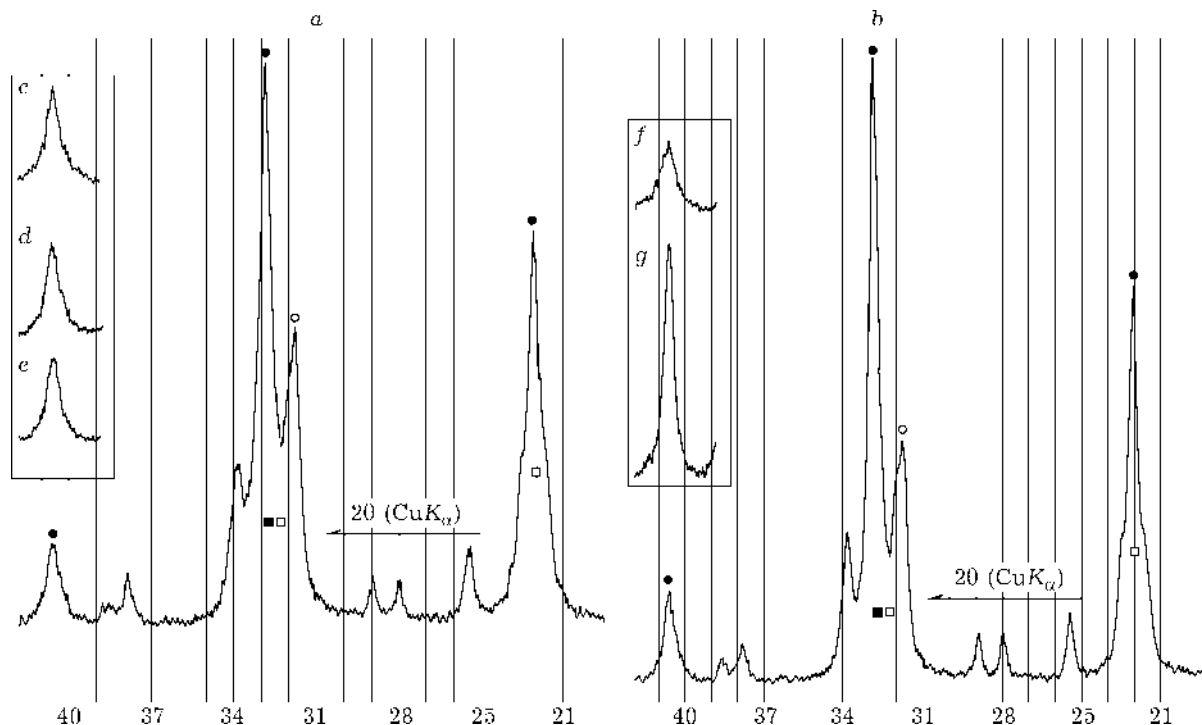


Fig. 6. XPA data on the dynamics of reaction (1d) and changes in CL depending on MA time  $\tau$ , s: a – 1800, b – 2100. Inserts show the reflections at  $2\theta = 40.65^\circ$  from the (111) plane for  $\tau$  equal to 600 (c), 900 (d), 3600 (e), 5400 (f), 300 s (g) magnification in the vertical direction is 3–4 times).

than  $\Psi(\tau = 900 \text{ s})$  (see Table 3). Further on, alternation of intensities of self-lining and mass transfer by milling bodies should occur; however, such a trend should get smoothed down and approach a definite equilibrium value while MA time increases; unfortunately, it is difficult to establish this equilibrium value theoretically. We recommend using  $\Psi_{\text{eq}}(\tau) = \Psi[\alpha(\tau_{\text{eq}}) = 0.5] \approx 0.0057$  as the equilibrium value.

#### Calculations according to the XPA data

The results of XPA of samples which were used by us both to estimate the kinetics of mechanically activated reaction (1a) and to estimate the size  $D$  of coherent lengths (CL) and deformations  $Y$  of the lattice of target nanometer-sized product thallium chloride (TlCl).

It may be established from Fig. 6 that the ratio  $\alpha(\tau = 2100 \text{ s})/\alpha(\tau = 1800 \text{ s}) \approx 0.31/0.23 \approx 1.3$ . If we use relative intensities  $I$  from planes (110) for TlCl ( $2\theta = 32.9^\circ$ ,  $d_{110} = 0.272 \text{ nm}$ ) and (200) for NaCl ( $2\theta = 31.7^\circ$ ,  $d_{200} = 0.282 \text{ nm}$ ), we obtain:  $I(\text{TlCl})/I(\text{NaCl}) \approx 1.9 = I(\tau = 1800 \text{ s})$  (see Fig. 6, a);  $I(\tau = 2100 \text{ s}) \approx 2.4$  (see Fig. 6, b). Therefore,  $I(\tau = 2100 \text{ s})/I(\tau = 1800 \text{ s}) \approx$

$2.4/1.9 \approx \alpha(\tau = 2100 \text{ s})/\alpha(\tau = 1800 \text{ s})$  (for example, see [9, 29]). However, monitoring of the kinetic curve  $\alpha(\tau, z^*)$  in Fig. 4 on the basis of XPA data is not so irrefragable because overlap of the reflections of the initial and final products within the region of  $2\theta$  angles under investigation causes a substantial increase in the deviation between the determinations of relative changes of  $\alpha(\tau, z^*)$  by means of conductometry and by means of XPA for MA time  $1800 \text{ s} > \tau > 2100 \text{ s}$ . Moreover, at the initial region of MA overlap of the reflections of initial and final reaction products is expressed in such a clear manner that the maximum  $I(\text{NaCl})$  shifts to the diffraction angle  $2\theta \approx 32^\circ$ . The reflection from (111) plane of TlCl does not overlap with other reflections of the reaction components (see Fig. 6). Further on, this fact is used in the present investigation.

In order to calculate the size  $D$  of particles (CL) and microdeformations of lattice  $Y$  from the XPA data, we applied widely known methods [22, 29–34] (Table 4).

1. Scherrer equation basing on the width  $B_s$  of the XPA reflection from (111) plane of TlCl for mechanically activated samples at the half

TABLE 4

Calculated changes in CL and microdeformations in TiCl lattice (reflection from the (111) plane) depending on MA time  $\tau$

Parameter	$\tau$ , s								
	300	600	900	1200	1800	2100	3600	5400	7200
$B$ , rad <sup>a</sup>	0.0056	0.0071	0.0078	0.0048	0.0089	0.0073	0.0090	0.0110	0.0029
$D$ , nm <sup>a</sup>	26	21	19	31	17	20	16	13	50
$B_i$ , rad <sup>b</sup>	0.009	0.011	0.012	0.011	0.013	0.010	0.012	0.014	0.006
$D$ , nm <sup>b</sup>	47	28	24	30	34	48	80	80	85
$Y$ , % <sup>b</sup>	0.0025	0.0026	0.0028	0.0031	0.0046	0.0038	0.0056	0.0075	0.0077

<sup>a</sup> According to Scherrer  $D = 0.9\lambda/B\cos\theta$  and Warren  $B^2 = B_s^2 - B_{st}^2$  equations.

<sup>b</sup> According to Foigt or integral intensity.

of their intensity and Warren equation, the standard broadening  $B_{st}$  of XPA reflections related to the instrument (the so-called instrumental broadening) was taken into account by the half-width of (222) line of the initial  $\text{Na}_2\text{SO}_4$  powder ( $2\theta = 38.6^\circ$ ,  $d_{222} = 0.233$  nm) (see Fig. 1) which is close in  $2\theta$  and  $d_{hkl}$  to the (111) reflection of TiCl.

2. Approximation over one Foigt line [32] assuming that the contribution into the line profile from  $D$  is described by Cauchy equation, from  $Y$  by Gauss equation, and the use of integral intensity of reflection  $B_i$ .

The use of equation  $B\cos\theta = (0.9\lambda/D) + Y\sin\theta$  [22] where  $\lambda$  is the wavelength of  $\text{CuK}_\alpha$  radiation which is 0.5418 nm, was hindered due to overlap of (110) reflections with the corresponding  $\text{Na}_2\text{SO}_4$  reflections (compare Figs. 5 and 6). Separation of the effects of  $D$  and  $Y$  using the second orders of reflections (222), (444) can give ambiguous picture due to their very weak intensity (high dispersion, distortion and/or multiphase composition of the material, redistribution of intensities due to texture [30]. As a rule [30, 31], with all the above-listed methods, unprocessed XPA spectra (originals recorded directly by a plotter) are used as illustrations; in the present work we did so, too (see Figs. 5 and 6).

A comment to Table 4 should be added (see also [34]). Underestimated and non-monotonous changes in crystallite size calculated using Scherrer equation without taking into account the effect of microdeformations  $Y$  on broadening of reflection (111) couldn't be considered to be correct. Taking into account  $Y$

crucially changes the character of  $D$  variation, which becomes expectable. At the initial stage of MA (10 min), the available shock-friction contacts between reagent particles in the initial mixture work; because of this, the CL is large and close to the values for traditional mechanochemical reactions [22, 24, 30]. With an increase in  $\tau$ , as a result of the formation of new contacts between reagents and the action of diluent particles ( $\text{Na}_2\text{SO}_4$ ), the CL decreases. Further increase in  $\tau$  should lead to an increase in CL as a result of mass transfer (generation of contacts between the nanometer-sized particles of the target reaction product TiCl), so  $D(\tau)$  function for  $\tau \approx 900$  s has a minimum and a continuous trend to increased for  $\tau > 900$  s. This occurs also after the reaction (1d) is formally completed for  $\tau > 6300$  s.

## CONCLUSIONS

Numerical modeling of the conditions of mechanosynthesis of nanoparticles by means of dilution with the final product is carried out. For experimental investigation of reaction (1d) as example, we confirmed the theoretical value of the parameter of molar dilution  $z = z_1^* = z^* = 11.25$ ; the kinetic curve of the reaction was obtained; the coefficient of mass transfer with the mobile milling bodies (ball load) in AGO-2 mill was determined; the size of CL blocks and microdeformations in the lattice of the target product were calculated. A satisfactory agreement of theoretical estimations with the experimental data,



available from literature and obtained experimentally, was achieved.

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