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# Kinetics of Two-Stage Mechanochemical Synthesis of Calcium Zirconate in $CaCO_3$–$ZrO_2$ System

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**Abstract**—Reaction of formation of calcium zirconate in $CaCO_3$–$ZrO_3$ system at 1:1 molar ratio is studied at 800, 850, and 900°C. Preliminary mechanoactivation of the reagents mixture in the centrifugal planetary mill was used. Obtained conversion data were analyzed using a macrokinetic model of two-stage mechanochemical synthesis applying the Jander and Zhuravlev–Lesokhin–Tempelman equations.

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Mechanochemical activation is an effective method of intensifying physicochemical processes involving solid substances (for example, dissolution, caking) as well as the solid-phase synthesis of compounds with different types of bonds (ionic, covalent, metal, etc.) [1–7]. For the acceleration of synthesis two versions of mechanochemical activation are used. The formation of substance may proceed quantitatively directly during the mechanical treatment of reagents in the activating mill. Such synthesis is called mechanochemical. If the reaction is not sensitive to the mechanical treatment, for example, because of thermodynamic limitations under the conditions of mechanochemical activation, a preliminary mechanochemical activation with the subsequent thermal treatment may be quite effective. In this case the mechanochemical synthesis is called a two-stage process.

Recently we have studied the kinetics of the formation of calcium zirconate in $CaCO_3$–$ZrO_2$ system at 1000-1300°C without mechanochemical activation [8]. The data reported on the effect of mechanochemical activation on this reaction are rather limited. Marchev et al. [9] showed the principle possibility of considerable decrease in temperature of synthesis of $CaZrO_3$ (to 900°C) by means of preliminary mechanochemical activation of initial reagents, but the kinetics of the process was not investigated. The aim of this work is the investigation of kinetic rules of two-stage mechanochemical synthesis of calcium zirconate in $CaCO_3$–$ZrO_2$ system. In the first stage a dosed mechanochemical activation of mixture of reagents is carried out. In this stage the conversion is low. In the second stage the quantitative formation of reaction products takes place due to the heating of mechanically activated mixture under the controlled conditions.

Strict description of kinetics of mechanochemical processes is very complicated. It requires a detailed consideration of dynamics of strain formation in the solid body. The latter process depends on many factors like the type of mechanical activator and the regime of its operation, the nature, size, and form of particles of the substance, etc. Especially complicated is the investigation of kinetics of relaxation processes like the formation of the new surface, the heat liberation, the formation of structure defects, the electronic excitation, the ionization, processes of mass transfer, and the chemical transformation proper [1–3, 10, 11].

Note also that during mechanochemical activation strains in the solid body act locally and have pulse character. Direct evaluation of pressures and temperatures arising during such treatment is very complicated. $P$ and $T$ gradients may be estimated by theoretical evaluation which is confirmed indirectly by the experiment, According to the calculations [12] in the centrifugal planetary mills in the course of contact of particles under treatment the short time pulse pressures reaching $10^9$–$10^{10}$ Pa appear. For the particles of the size ~1 μm during $10^{-8}$–$10^{-9}$ s tempera-

ture flashes $\Delta T \sim 10^3$ K arise in the localization range ~10 $n_m$. Main part of substance in the course of mechanochemical activation remains relatively cold. The background temperature in the mill does not exceed 350–400 K.

In this work the kinetics of two-stage mechanochemical synthesis of $CaZrO_3$ in $CaCO_3$–$ZrO_2$ system are studied using the macroscopic approximation [13]. Parameters of macrokinetic model are the values averaged over the volume of mechanoreactor. They include mean values of conversion, temperature, size of particles, excessive energy. For the two-stage synthesis the problem simplifies because the accumulation of excessive energy and the chemical transformation are separated.

According to macrokinetic model [13] the intensifying of chemical reaction resulting from mechanochemical activation in general case takes place due to the three main factors, that is, the size-structural, kinetic, and temperature factors. The appearance of the first one is connected with the fact that during the mechanochemical treatment of powder mixture grinding takes place which is accompanied by the increase in the interphase surface, the most important parameter determining the rate of heterogenic reaction. Simultaneously the scale of heterogeneity (the characteristic size of particles) determining the time of mass transfer of solid phase reagents to one another diminishes. Together with the decrease in the scale of heterogeneity the microstructure of powder mixture complicates. The formation of microcomposites in the volume of which the reaction products are formed in the case of one-stage mechanochemical synthesis can take place.

At the increase in duration of mechanochemical activation (the dose of supplied mechanical energy) the dispersion rate diminishes. It is connected with the increase in plastic flow of substance, the process connected with the intense formation of defects. Kinetic factor becomes apparent due to the accumulation of defects in crystalline lattice leading to accumulation of excessive energy that decreases the effective activation energy of the chemical transformation. While heating of the preliminary mechanoactivated mixture the reason of the acceleration of chemical reaction may originate also from the heat evolution resulting from the exothermic chemical transformation and dissipative heat evolution due to relaxation of structural irregularities induced by mechanochemical treatment. It is the manifestation of temperature factor of the chemical reaction intensification [13].

**Table 1.** Dependence of specific surface ($S_{sp}$) of the mixture ($CaCO_3$ + $ZrO_2$), of the specific surface of $ZrO_2$ in the mixture, and the degree of transformation of zirconium dioxide to calcium zirconate ($\alpha_{ma}$) on the duration of mechanochemical activation and the dose of supplied mechanical energy ($D_e$)

| Time of mechanochemical activation, min | 0 | 2 | 6 | 10 |
|---|---|---|---|---|
| $D_e$, kJ $g^{-1}$ of mixture | 0 | 3.6 | 10.8 | 18 |
| $S_{sp}$ ($CaCO_3$ + $ZrO_2$), $m^2$ $g^{-1}$ | 5.4 | 6.2 | 4.2 | 3.9 |
| $S_{sp}$ ($ZrO_2$), $m^2$ $g^{-1}$ | 9.8 | 17.4 | 25.6 | 28.9 |
| $\alpha_{ma}$, parts of unit | 0 | 0.0192 | 0.0235 | 0.0238 |

In the preliminary experiments it was established that the combined mechanochemical activation of $CaCO_3$ and $ZrO_2$ from the point of view of degree of formation of $CaZrO_3$ at the subsequent calcination is 3–4 times more effective than separate mechanochemical activation at the same power consumption and subsequent mixing of reagents. As known, the results of mechanochemical activation under the same conditions may depend on the size (or mass) of balls in the mill [2]. It was found that in this case the size of balls (4 or 8 mm) practically did not influence the characteristics of mixture (specific surface, amorphization degree) and the degree of formation of calcium zirconate during subsequent calcination. In further experiments joint mechanochemical activation of calcium carbonate and zirconium dioxide was carried out using 8 mm balls.

It follows from the data presented in Table 1 on the specific surface of $CaCO_3$ + $ZrO_2$ mixture depending on the duration of mechanochemical activation that dispersion proceeds in the course of first two min of mechanochemical treatment, and then due to prevailing processes of aggregation the specific surface ($S_{sp}$) of the mixture considerably decreases. In the Table 1 the values of $S_{sp}$ of zirconium dioxide in the mechanoactivated mixture and in the starting $ZrO_2$ are also presented. They show that monotonous decrease of size of this component in the course of mechanochemical activation takes place. We showed [8] that $ZrO_2$ sample with $S_{sp}(ZrO_2)$ 9.8 $m^2$ $g^{-1}$ which was used in this work as well consisted of the aggregates of particles stable to ultrasound treatment. The intense mechanical treatment of ($CaCO_3$ + $ZrO_2$) mixture in

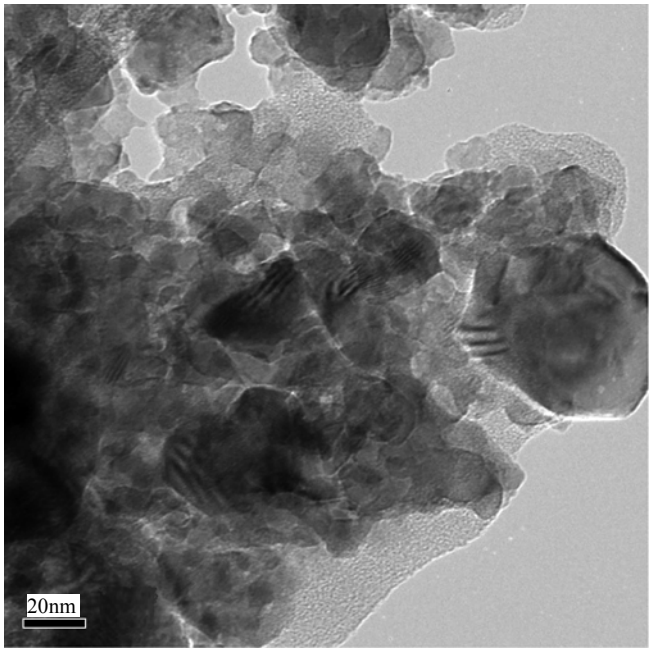


**Fig. 1.** TEM image of powder ($CaCO_3$ + $ZrO_2$) after 10 min of mechanochemical treatment.

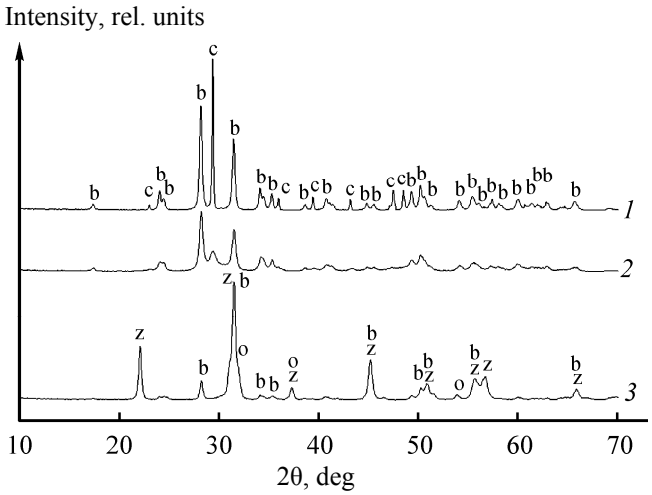


**Fig. 2.** X-ray photograph of samples: (*1*) starting mixture ($CaCO_3$ + $ZrO_2$), (*2*) sample 1 after 10 min of mechanochemical activation, (*3*) sample 2 after calcinations at 900°C for 1 h. Solid phases: (b) $ZrO_2$ (baddeleite), (c) $CaCO_3$ (calcite), (o) CaO, (z) $CaZrO_3$.

the planetary mill not only destroyed the aggregates, but also the grinding of primary particles took place. Data on specific surface presented in Table 1 indicate that the increase in the dispersity of zirconium dioxide on the background of decrease in $S_{sp}$ of the mixture during mechanochemical activation is accompanied by the increase in interphase surface due to smearing of more pliable calcium carbonate on $ZrO_2$ particles and the formation of secondary aggregates. This suggestion was confirmed by the data of transmission electron microscopy. In Fig. 1 TEM image of a mixture of calcium carbonate and zirconium dioxide after 10 min of mechanochemical activation is presented. It is clearly seen that dark particles of zirconium dioxide are joined in aggregates with light grey amorphized substance. According to the data of energy dispersion analysis the latter one is calcium carbonate. The greater amorphization of $CaCO_3$ as compared to $ZrO_2$ is illustrated by X-ray photograph of a mixture of reagents after mechanochemical activation (Fig. 2). The increase in the interphase surface is probably the reason of significantly higher effectiveness of joint mechanochemical activation as compared to separate one from the point of view of the yield of calcium zirconate at the subsequent heating.

In Table 1 the values of dose of supplied mechanical energy for the used operating regime of planetary mill evaluated according to [14, 15] and the conversion of zirconium dioxide to calcium zirconate ($\alpha_{ma}$) in the course of mechanochemical activation are presented. Note that standard Gibbs energy of the reaction is a large positive value, $\Delta_r G^0_{298}$ = +96 kJ mol$^{-1}$ [16].

$$CaCO_3 + ZrO_2 = CaZrO_3 + CO_2.$$

Considering this fact and also the rules found in the investigation of mechanochemical interaction of barium carbonate with metal oxides of IV–VI groups of periodical system [17] the low values of $\alpha_{ma}$ for $CaCO_3$–$ZrO_2$ system (Table 1) are quite expectable. Before consideration of the main data on the synthesis of calcium zirconate in the stage of heating of mechanoactivated mixtures it is interesting to analyze from the point of view of energy approach [3, 18] on the basis of data of Table 1 the specific features of the initial formation of $CaZrO_3$ in low yield during treating the reagents in the mill.

According to [3, 18] the possibility of mechanochemical synthesis at low temperature ($T < 0.3T_m$), when the diffusion rate is low, arises from deformational mixing of reagents with the subsequent formation of reaction product under the joint action of mechanical and chemical forces. Deformational stirring involves diminishing the size of particles, the appearance and the growth of interphase boundaries, the formation of surface compounds on them and

penetrating of atoms through the interphase boundarys with the formation of bulk product. These and some other processes taking place during mechanical synthesis may be divided in two groups, that is, thermal and non-thermal ones. Thermally activated chemical reactions and diffusion correspond to thermal processes. The dispersion of solid body with the formation of fresh surface, plastic deformation, deformational mixing of components of the system including formation of reaction zones are non-thermal processes because they proceed due to expenditure of mechanical energy. The ratio of these two types of processes may vary depending on the nature of reagents, the type and energy strain of mechanical treatment, and some other factors. For thermal processes reaction coordinates are time and rate, and for non-thermal, the dose of consumed energy $D_e$ and the energy yield, that is the ratio of amount of converted substance to the dose of energy. On the basis of experimental data on the consumed energy, the area of contact of reagents, and the degree of conversion it is possible to establish which of two types of the above-mentioned processes is dominant. With this purpose at the assumption of one-sided penetration through the interphase surface we calculated the mean number of monolayers of mobile component $n_m$ that passed through the unit of contact area due to consumption of dose $D_e$ (kJ $g^{-1}$ of mixture) [18]:

$$n_m = G_o D_e / N_s,$$

where $G_o$ is the coefficient equal to the number of moles of component passing through the unit of contact area at the expenditure of a unit of dose of mechanical energy (mol g $kJ^{-1}$ $m^{-2}$); $N_s$ is the surface concentration of mobile reagent (mol $m^{-2}$). For the system under consideration the mobile component is calcium oxide formed during partial dissociation of calcite in the course of mechanochemical activation, and intherphase surface is set to be equal to the surface of $ZrO_2$ in the mixture. Considering that $N_s \sim 10^{-5}$ mol $m^{-2}$ [18] $n_m$ values calculated on the basis of data of Table 1 and the composition of starting mixture vary in the range $(4–5)\times10^{-1}$. Values $n_m$ are < 1 which indicates the proceeding of the reaction only on $ZrO_2$ surface due to the deformational stirring. Data of Table 1 permit also the evaluation of the work of the formation of zirconium dioxide surface which increases from 0.5 to 0.9 kJ $m^{-2}$ at the increase in duration of mechanochemical activation from 2 to 10 min.

Let us consider the processes taking place in the second stage of the synthesis. According to thermal analysis data the preliminary treatment of $CaCO_3$ + $ZrO_2$ mixture in a mill does not influence significantly the character of differential scanning calorimetry, thermogravimetry, and differential thermogravimetry curves (not presented). For all the mechanically activated mixtures the temperature of the maximum of *endo*-effect of $CO_2$ removal on differential scanning calorimetry curve coincides with the temperature of maximum value of the rate of mass loss. It is located in the range 838–845°C which is lower than the analogous value for the mixture not subjected to mechanochemical activation (856°C [8]). According to the thermogravimetry data the mass loss of mechanoactivated mixtures due to thermolysis of $CaCO_3$ finishes in the range 850–880°C what agrees with the absence of reflexes of calcite in the X-ray photographs of samples after calcinations at 900°C (Fig. 2). The presence of pea*k*s of calcium oxide in the X-ray photographs of calcinated mechanoactivated mixtures (Fig. 2) permits a conclusion that similar to the mixture which was not subjected to mechanochemical activation [8] the synthesis of calcium zirconate proceeds in two stages. At first decomposition of $CaCO_3$ takes place, and then CaO reacts with $ZrO_2$ to give $CaZrO_3$.

Experimental procedure for obtaining data on the degree of formation of calcium zirconate is described in [8]. It is based on a controlled heating of about 1 g of a mixture to the given temperature and keeping it at this temperature for a definite time. Effective duration of isothermal handling $\tau_{ef}$ which is used as a coordinate in kinetic analysis is evaluated by a relationship:

$$\tau_{ef} = \Delta\tau_{ef} + \tau_{is},$$

where $\tau_{is}$ is the duration of heating at constant temperature, $\Delta\tau_{ef}$ is correction additive which is calculated from the known dependence of reaching the isothermal regime by a furnace [8].

In Fig. 3 experimental degree of transformation α minus the amount of $CaZrO_3$ formed during mechanochemical activation as a function of $\tau_{ef}$ at 800, 850, and 900°C is presented. These data were used in the kinetic analysis. According to macrokinetic model of mechanochemical synthesis [13] the rate of the formation of product from a mixture of two reagents is expressed by the Eq. (1)

$$d\alpha/d\tau = k(T)f(\alpha)F(S). \quad (1)$$

Here α is the degree of transformation, that is, a mass part of product in relation to the sum of the mass of

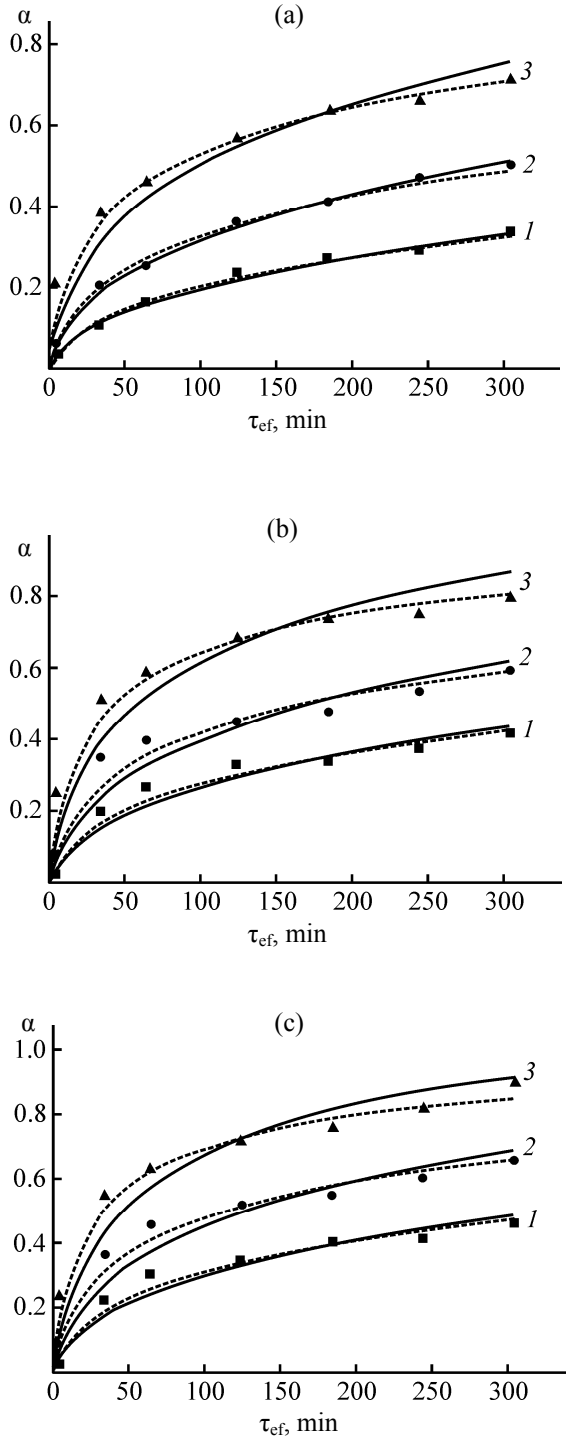


**Fig. 3.** Degree of transformation (α) as a function of effective duration of isothermal keeping ($\tau_{ef}$) of a mixture at a temperature: (*1*) 800°C, (*2*) 850°C, (*3*) 900°C. Starting specific surface of $ZrO_2$ is 9.8 $m^2\ g^{-1}$. Experimental data are marked by symbols, continuous lines correspond to calculations according to the Jander equation, dotted lines correspond to calculations according to the Zhuravlev–Lesokhin–Tempelman equation. Time of preliminary mechanic activation, min: (a) 2, (b) 6, and (c) 10.

reaction mixture and the product. For the stoichiometric mixture of reagents it coincides with the degree of transformation of zirconium dioxide to zirconate. $T$ is temperature, $k(T) = A\exp(-E_a/rt)$, $A$ and $E_a$ are the preexponent multiplier and the activation energy of the reaction, $R$ is gas constant, $f(\alpha)$ is the function characterizing the kinetic rule of the reaction, $F(S)$ is the dimensionless function reflecting the effect of interphase reaction surface (in our case $ZrO_2$ surface) on the reaction rate.

Activation energy is presented as follows:

$$E_a = E_a^0 - \varphi_e. \quad (2)$$

Here $E_a^0$ is the activation energy of the reaction in the absence of structural defects, that is, for the starting system which was not exposed to mechanochemical activation, $\varphi_e$ is the part of excess energy accumulated in the course of mechanochemical activation as structure defects and decreasing starting activation energy. In the course of mechanochemical activation the excess energy is accumulated by $CaCO_3$ as well as by $ZrO_2$. As it was marked above, the formation of calcium zirconate begins after complete decomposition of calcite to CaO. It is suggested that in agreement with the thermal analysis data excess energy accumulated by Ca carbonate is consumed to decrease the temperature (and the energy consumption) of its decomposition. That is why (CaO + $ZrO_2$) is the reaction mixture, and all its excessive energy is accumulated by zirconium dioxide. It is expressed by the equation:

$$\varphi_e = a_e c_z \varphi(ZrO_2). \quad (3)$$

Here $a_e$ is coefficient, $c_z = 0.6872$ is mass part of $ZrO_2$ in its stoichiometric mixture with CaO, $\varphi(ZrO_2)$ is the excessive energy accumulated by $ZrO_2$.. $a_e$ Value is set equal to 1. This means that the annealing of defects in zircomium dioxide in the course of heating is insignificant and the product ($CaZrO_3$) does not inherit structural defects and the excess energy of $ZrO_2$ connected with them. In another words, all energy accumulated by zirconium dioxide is consumed in the acceleration of the chemical transformation. The assumption on the insignificance of relaxation of structural defects in $ZrO_2$ while heating agrees with evaluation of relative broadening of peaks in the X-ray photographs of zirconium dioxide. With this purpose X-ray photographs were taken of $ZrO_2$ samples (not presented) obtained after treating with hydrochloric acid of calcinated mechanoactivated mixtures in the course of their analysis (see Experimental). The

obtained data show that while heating during 5 h at 800–900°C integral width of main diffraction maximum of $ZrO_2$ decreased by no more than 10%.

For the evaluation of dimensionless $F(S)$ function characterizing specific surface (average size of particles of $ZrO_2$) in the reaction mixture $S_{sp}$ was measured for the same samples of zirconium dioxide for which broadening of peaks in X-ray photographs was evaluated. The obtained data show that $S_{sp}$ of $ZrO_2$ while heating to some extent decreased as compared to the starting meanings of this value for mechanoactivated mixtures presented in the Table 1. To the first glance this result disagrees with the notion that in the course of the reaction the average size of $ZrO_2$ particles must decrease, and $S_{sp}(ZrO_2)$ value must grow respectively. At the same time considering the polydispersity of composition a decrease in $S_{sp}(ZrO_2)$ can take place due to the higher reactivity of small particles of zirconium dioxide in mechanoactivated mixture. That means that they must disappear quickly. It cannot be excluded that aggregation of $ZrO_2$ particles may be the additional factor.

It was assumed that after 2, 6, and 10 min of mechanochemical activation at heating of mixtures $S_{sp}$ of $ZrO_2$ in them remained the same. It was 16.4±0.5, 20.3±0.7, and 24.6±0.9 $m^2\ g^{-1}$ respectively. These values were obtained by averaging of $S_{sp}(ZrO_2)$ for the above-mentioned samples. Hence, for each time of mechanochemical activation $F(S)$ is included in the Eq. (1) as a coefficient. For the diffusion models of solid phase reactions without using mechanochemical activation $F(S) \sim 1/r^2 \sim (S_{sp})^2$ where $r$ and $S_{sp}$ are the mean radius of particles and the specific surface of covered reagent [1]. For mechanoactivated mixtures $F(S)$ is reciprocally proportional to the first degree of linear size of obtained microcomposites [13]. Let us set that $F(S) = [uS_s(ZrO_2)]q$ where $q$ is a parameter and u is normalizing factor equal to 1 g $m^{-2}$.

As enthalpy of the reaction $CaO + ZrO_2 = CaZrO_3$ in the temperature range under study is relatively small (–31 kJ $mol^{-1}$ [8]) and the process is prolonged, the temperature factor of acceleration of synthesis of calcium zirconate may be neglected.

Considering the relationship (2) and the assumption for $F(S)$ Eq. (1) must have the following shape.

$$d\alpha/d\tau = A[uS_{sp}(ZrO_2)]^q f(\alpha)\exp(-E_o/RT)\exp(\varphi_e/RT) = k_S(T)f(\alpha). \quad (4)$$

Here $k_s(T)$ is the rate constant depending on the interphase reaction surface. Equation (4) may be also presented as follows

$$d\alpha/d\tau = k_S^0(T)f(\alpha)\exp(\varphi_e/RT), \quad (5)$$

where $k_s^0(T)$ is the rate constant in the absence of structural defects ($\varphi_e = 0$), that is, in the case when the mixture of starting reagents was not subjected to mechanochemical activation and had the same interphase surface as after mechanochemical activetion. Rate constants $k_s(T)$ and $k_s^0(T)$ are connected by the relationship:

$$k_S(T) = k_S^0(T)\exp(\varphi_e/RT). \quad (6)$$

The kinetic analysis of the degree of formation of calcium zirconate in $CaCO_3$–$ZrO_2$ system without mechanochemical activation showed [8] that the experimental data are best of all described by the Jander and Zhuravlev–Lesokhin–Tempelman diffusion equations. These equations quite adequately describe the experimental data also for the system where the components were exposed to mechanochemical activation. In Tables 2 and 3 $k_s(T)$ values calculated using respectively Jander and Zhuravlev–Lesokhin–Tempelman equations are presented. Errors in Tables 2 and 3 correspond to root-means square deviations. The calculation of $k_s(T)$ was carried out analogously to the systems without mechanochemical activation [8] by minimization of the sum of squares of deflections of the experimental α values from that calculated by means of the Eqs. (7), (8).

$$\alpha = 1 - [1 - \sqrt{k_{S(Jander)}\tau}]^3, \quad (7)$$

$$\alpha = 1 - [1/\{\sqrt{k_{S(Zhuravlev–Lesokhin–Tempelman)}\tau} + 1\}^3]. \quad (8)$$

The non-linear root-mean-square method was used [20]. Equations (7) and (8) are integral forms of general Eq. (4). In Tables 2 and 3 the activation energies $E_a$ obtained by linearization of $k_s(T)$ values in the Arrhenius coordinates and the corresponding correlation coefficients $R_k$ which together with the $R_k$ values for $k_s(T)$ may be regarded as the criteria of applicability of kinetic equations [21] are presented. From the results listed in Tables 2, 3 it follows that the Zhuravlev–Lesokhin–Tempelman equation better describes degrees of transformation in the course of isothermal heating of mechanochemically activated mixtures. Yet the correspondence of temperature dependence of calculated rate constants to the strait line in the Arrhenius coordinates is more accurate at the use of the Jander equation.

**Table 2.** Kinetic parameters of the formation of $CaZrO_3$ with preliminary mechanochemical activation calculated by means of Jander equation

| Time of mechanochemical activation, min | $t$, °C | $k_S$, $min^{-1}$ | $R_k$ for $k_S$ | $\Delta\tau_{ef}$, min | $E_a$, kJ $mol^{-1}$ | ln $A$ | $R_k$ for $E_a$ |
|---|---|---|---|---|---|---|---|
| 2 | 800 | $(5.13\pm0.23)\times10^{-5}$ | 0.9954 | 3.54 | 228±12 | 15.7±1.3 | –0.9987 |
| | 850 | $(1.46\pm0.03)\times10^{-4}$ | 0.9990 | 3.77 | | | |
| | 900 | $(4.56\pm0.41)\times10^{-4}$ | 0.9835 | 3.91 | | | |
| 6 | 800 | $(9.98\pm0.86)\times10^{-5}$ | 0.9823 | 3.59 | 215±20 | 14.8±2.1 | –0.9957 |
| | 850 | $(2.47\pm0.28)\times10^{-4}$ | 0.9711 | 3.86 | | | |
| | 900 | $(7.80\pm1.02)\times10^{-4}$ | 0.9718 | 4.01 | | | |
| 10 | 800 | $(1.30\pm0.12)\times10^{-4}$ | 0.9791 | 3.59 | 215±12 | 15.1±1.3 | –0.9985 |
| | 850 | $(3.44\pm0.34)\times10^{-4}$ | 0.9805 | 3.86 | | | |
| | 900 | $(1.02\pm0.11)\times10^{-3}$ | 0.9854 | 4.01 | | | |

**Table 3.** Kinetic parameters of formation of $CaZrO_3$ with preliminary mechanochemical activation calculated by means of Zhuravlev–Lesokhin–Tempelman equation

| Time of mechanochemical activation, min | $t$, °C | $k_S$, $min^{-1}$ | $R_k$ for $k_S$ | $\Delta\tau_{ef}$, min | $E_a$, kJ $mol^{-1}$ | ln $A$ | $R_k$ for $E_a$ |
|---|---|---|---|---|---|---|---|
| 2 | 800 | $(6.31\pm0.36)\times10^{-5}$ | 0.9939 | 3.42 | 273±21 | 20.8±2.3 | –0.9970 |
| | 850 | $(2.07\pm0.09)\times10^{-4}$ | 0.9972 | 3.49 | | | |
| | 900 | $(8.59\pm0.48)\times10^{-4}$ | 0.9964 | 3.60 | | | |
| 6 | 800 | $(1.35\pm0.11)\times10^{-4}$ | 0.9885 | 3.42 | 269±31 | 21.2±3.3 | –0.9936 |
| | 850 | $(4.02\pm0.39)\times10^{-4}$ | 0.9864 | 3.51 | | | |
| | 900 | $(1.78\pm0.11)\times10^{-3}$ | 0.9966 | 3.63 | | | |
| 10 | 800 | $(1.83\pm0.17)\times10^{-4}$ | 0.9864 | 3.42 | 272±20 | 21.8±2.1 | –0.9974 |
| | 850 | $(6.04\pm0.46)\times10^{-4}$ | 0.9929 | 3.49 | | | |
| | 900 | $(2.47\pm0.17)\times10^{-3}$ | 0.9970 | 3.60 | | | |

For both equations within the limits of evaluation error no monotonous decrease of $E_a$ at the increase in duration of mechanochemical activation was found [see Eq. (2)], and in the case of the use of Zhuravlev–Lesokhin–Tempelman equation the activation energy is practically constant (Table 3). In connection with that it must be noted that each $E_a$ value in the Tables 2, 3 is calculated on the basis of $k_s(T)$ rate constants corresponding to different interphase surfaces. More sensitive characteristic reflecting energy variation in reagents in the course of mechanochemical activation is the excess energy $\varphi_e$ which can be found on the basis of Eq. (6) using evaluated $k_s(T)$ constants (Tables 2, 3) according to following scheme. By means of extrapolation of data for the systems without mechanochemical activation it is possible to calculate $k^0_{S1}(T)$ values for 800, 850, and 900°C. Index SI in the rate constant indicates the difference in $S_{sp}(ZrO_2)$ [8] from that in mechanochemically activated systems what is necessary to consider while evaluating $\varphi_e$. In this case it follows from Eqs. (4) and (6):

$$\varphi_e = RT\ln\{[k_S(T)/k^0_{S1}(T)]\cdot[uS_{1s}(ZrO_2)]^{q1}/[uS_{sp}(ZrO_2)]^q\}. \quad (9)$$

In Eq. (9) $S_{1s}(ZrO_2)$ is 0.79 $m^2\ g^{-1}$ [8], $S_{sp}(ZrO_2)$ are equal to 16.4, 20.3, and 24.6 $m^2\ g^{-1}$ for 2, 6, and 10 min of mechanochemical activation respectively, $q$ = 1 and $q1$ = 2 as it follows from the above considerations. Values $\varphi_e$ calculated in this way are listed in Table 4 from which it follows that the accumulated energies grow monotonously with the increase in duration of mechanochemical activation in the ranges 23–27 and 28–34 kJ $mol^{-1}$ while using Jander and Zhuravlev–Lesokhin–Tempelman equations respectively. Note that if the parameter $q$ is set equal to 2 as for the systems without mechanochemical activation, it leads to negative $\varphi_e$ values having no physical sense.

From Eqs. (4)–(6) it follows that calculation of degree of the reaction proceeding in the two-stage

**Table 4.** Calculated values of energy accumulated during mechanochemical activation $\varphi_e$, and Gibbs energy of amorphization of zirconium dioxide $\Delta G_{am\text{-}cr}(ZrO_2)$

| Model | Time of mechanochemical activation, min | $\varphi_e$, kJ mol$^{-1}$ | $D_{am}$[a] | $\Delta G_{am\text{-}cr}(ZrO_2)$, kJ mol$^{-1}$ |
|---|---|---|---|---|
| Jander | 2 | 22.9±0.9 | 0.44±0.01 | 76±3 |
| | 6 | 26.2±0.9 | 0.49±0.01 | 78±3 |
| | 10 | 27.2±0.5 | 0.51±0.01 | 78±2 |
| Zhuravlev–Lesokhin–Tempelman | 2 | 28.0±1.0 | 0.44±0.01 | 93±4 |
| | 6 | 32.6±1.0 | 0.49±0.01 | 97±4 |
| | 10 | 34.2±0.9 | 0.51±0.01 | 98±3 |

[a] $D_{am}$ is the degree of amorphization of $ZrO_2$ in the course of mechanochemical activation.

mechanochemical synthesis may be carried our using 4 parameters. They include excess energy $\varphi_e$, interphase surface of mechanoactivated mixture, and also the rate constant $k^0_s(T)$ and interphase surface value corresponding to it which were evaluated for the system that was not subjected to mechanochemical activation. For the evaluation of excess energy accumulated by zirconium dioxide in the course of mechanochemical activation the following relationship was used [22]:

$$\varphi(ZrO_2) = D_{am}(ZrO_2)\Delta G_{am\text{-}cr}(ZrO_2). \quad (10)$$

Here $\Delta G_{am\text{-}cr}(ZrO_2)$ is the change in Gibbs energy at the transfer from crystalline $ZrO_2$ to the completely amorphous state. $D_{am}(ZrO_2)$ is the degree of amorphization of $ZrO_2$ in the course of mechanochemical activation. The standard amorphization enthalpy of monoclinic $ZrO_2$ obtained by the dissolution calorimetry method $\Delta H_a(ZrO_2)_{298}$ is reported to be equal to 58±3.3 kJ mol$^{-1}$ [23]. The entropy alteration according to [22] may be evaluated as follows:

$$\Delta S_{am\text{-}cr}(ZrO_2)_{298} \approx \Delta H_m(ZrO_2)/T_m,$$

where $\Delta H_m(ZrO_2)$ = 87 kJ mol$^{-1}$ is the heat of melting, and $T_m$ = 2983 K is the melting point of zirconium dioxide respectively [24]. Thus it can be found that $\Delta G_{am\text{-}cr}(ZrO_2)_{298} \approx 50$ kJ mol$^{-1}$. Using Eqs. (3) and (10) the same value can be calculated from $\varphi_e$ values (Table 4) and amorphization degree of $ZrO_2$ which was evaluated by the formula [25]:

$$D_{am} = 1 - [(U_o/I_o)(I/U)]. \quad (11)$$

Here $I$ and $I_0$ are integral intensities of main peak of X-ray diffraction for the mechanoactivated and standard $ZrO_2$; $U$ and $U_0$ are the corresponding base lines. For each time of mechanochemical activation $I$ values were found by averaging of this value for the above-mentioned $ZrO_2$ samples obtained after treating calcinated mechanochemically activated samples with hydrochloric acid. Starting $ZrO_2$ calcinated at 1300°C for 12 h was used as standard zirconium dioxide. As for mechanochemically activated $ZrO_2$ overlapping of neighboring reflexes took place due to their broadening, for their separation approximating Voigt pseudofunction was used. The latter is superposition of Lorentz and Gauss functions [26]. In the Table 4 for each time of mechanochemical activation mean degrees of amorphization $D_{am}(ZrO_2)$ are presented as well as $\Delta G_{am\text{-}cr}(ZrO_2)$ values calculated with their use. Note that as well as the values of energy, accumulated in the course of mechanochemical activation $\varphi_e$ the obtained $\Delta G_{am\text{-}cr}(ZrO_2)$ values depend on the type of chosen kinetic equation. For the Jander and Zhuravlev–Lesokhin–Tempelman equations the latter are 77±3 and 94±4 kJ mol$^{-1}$ respectively which significantly exceeds $\Delta G_{am\text{-}cr}(ZrO_2)$ value found from the data [22–24]. It shows on the necessity of improving the model and search for alternative approaches to evaluation of excess energy, for example, on the basis of calorimetric measurements for the products of mechanochemical activation [27]. The larger $\Delta G_{am\text{-}cr}(ZrO_2)$ values obtained from kinetic data may be due to the fact that while decomposition of $CaCO_3$ some part of energy accumulated during mechanochemical activetion is inherited by calcium oxide.

For the evaluation of the possibility using this version of simplified macrokinetic model for predictiton of course of the reaction under investigation an additional control experiment of mechanochemical activation of stoichiometric mixture of $CaCO_3$ with $ZrO_2$ sample with the specific surface 0.79 m$^2$ g$^{-1}$, that is, 10 times lower than the sample used in the above-described experiments (Table 1) was carried out. The

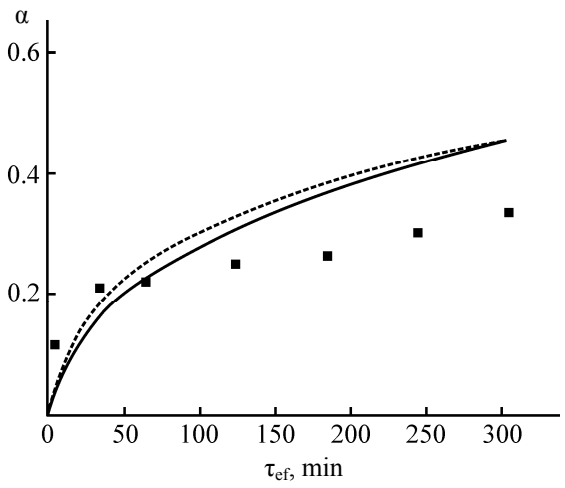


**Fig. 4.** Degree of transformation as a function of effective duration of isothermal keeping ($\tau_{ef}$) of $CaCO_3$ + $ZrO_2$ mixture at 900°C. Starting specific surface of $ZrO_2$ is 0.79 $m^2\ g^{-1}$. (Signs) show experimental data, (continuous lines) correspond to calculations according to the Jander equation, (dotted lines) correspond to calculations according to the Zhuravlev–Lesokhin–Tempelman equation. Time of preliminary mechanic activation 10 min.

process of mechanochemical activation in the course of 10 min and the procedure of heating of mechanoactivated mixture at 900°C corresponded to the previously performed experiments. The value of $\Delta\tau_{ef}$ = 3.5 min was found by interpolation of the data found in the course of previous experiments. The average value of $S_{sp}(ZrO_2)$ = 5.3 $m^2\ g^{-1}$ set as a value of interphase surface in the mixture and the amorphization degree $D_{am}(ZrO_2)$ = 0.385 were found as described above.

For the calculation of degree of the reaction proceeding according to the equations (7) and (8) the values of rate constants calculated as follows were used. From the data for the system without using mechanochemical activation rate constants $k^0_{S1(Jander)} = 1.63\times10^{-6}$ and $k^0{}_{S1(Zhuravlev–Lesokhin–Tempelman)} = 1.48\times10^{-6}$ for 900°C were calculated which corresponded to the $S_{s1}$ ($ZrO_2$) = 0.79 $m^2\ g^{-1}$ [8]. Excess energies $\varphi_e$ were calculated by the formula (3), (10), and (11). $\Delta G_{am\text{-}cr}(ZrO_2)$ were set equal to 77±3 and 96±4 kJ $mol^{-1}$ for the Jander and Zhuravlev–Lesokhin–Tempelman equations respectively (Table 4). Values $k_s$ which were substituted in Eqs. (7) and (8) were evaluated from the relationship (12).

$$k_S = k^0_{S1}\{[uS_{sp}(ZrO_2)]/[uS_{s1}(ZrO_2)^2]\}\exp[\varphi_e/(R\cdot1173)]. \quad (12)$$

Here $S_{s1}(ZrO_2)$ = 0.79 $m^2\ g^{-1}$, $S_{sp}(ZrO_2)$ = 5.3 $m^2\ g^{-1}$. The obtained values of rate constants are equal to $k_{s(Jander)} = 1.11\times10^{-4}$ and $k_{s(Zhuravlev–Lesokhin–Tempelman)} = 1.69\times10^{-4}$. In the Fig. 4 the calculated α values are presented together with the data of control experiment. Results of calculations using Jander and Zhuravlev–Lesokhin–Tempelman equations practically coincide. Considering the complex character of the object under study the agreement of the control experiment and the calculations with the consideration of the set assumeptions must be admitted as satisfactory.

On the whole it can be concluded that the model [13] is quite applicable for kinetic analysis of data of the two-stage mechanochemical reactions in macroscopic approximation. For exact quantitative prediction it is necessary to consider the dynamics of such factors as the value of accumulated energy, the interphase surface, etc., as well as heterogeneity of the system, for example polydispersity and different reaction rate in different parts of the volume, that is, to include in consideration the processes on meso- and microlevels (on separate particles and contact spots) [13]. It requires the introduction of new parameters and substitution of coefficients with functional dependences. Their pattern must be chosen on the basis of thorough investigation of physicochemical processes taking place on both stages of synthesis with the consideration of specific features of the reaction under study.

## EXPERIMENTAL

Two samples of zirconium dioxide of monoclinic modification (baddeleite) of chemically pure grade and calcium carbonate of pure for analysis grade were used in the experiments. $ZrO_2$ samples with the specific surface 9.8±0.5 and 0.79 $m^2\ g^{-1}$ were obtained by calcination of starting reactive zirconium dioxide at 600 and 1300°C respectively in the course of 12 h. According to X-ray spectral analysis $HfO_2$ content with respect to the sum of ($ZrO_2$+$HfO_2$) in the sample of zirconium dioxide was 0.11 mass %. Calcium carbonate was dried at 110°C for 24 h.

Starting mixtures containing $ZrO_2$ and $CaCO_3$ in 1:1 molar ratio were prepared by joint treating of calculated batches of reagents in the Fritsch Pulverisette 2 mechanical mortar in the regime of mixing, that is when the clamp of pestle to the mortar is the smallest, in the course of 4 h. The degree of uniformity of mixture was controlled by the constancy of content of volatile component ($CO_2$) in it, and its correspondence to the calculated value. The content of

$CO_2$ was evaluated from the loss of mass while calcinations of four parallel batches for 3 h at 1000°C.

Mechanochemical activation was carried out in the AGO-2 [2] laboratory centrifugal planetary mill at the centrifugal factor 40 g. Steel balls of 8 mm diameter, 200 g, and 10 g of sample were placed in a drum. After each two min of mechanochemical activation the mill was switched off and the load was constrainedly mixed. With the purpose of minimization of the amount of finely dispersed iron formed due to self abrasion of the material of mill the drums and balls were lined according to [28].

Calcination of mixtures of zirconium dioxide and calcium carbonate was carried our in air at 800, 850, and 900°C in the SNOL 6.7/1300 electric furnace. Each point was evaluated according to the results of 2–3 parallel probes. In the period of time between calcination and analysis the batches were maintained in a desiccator. Bulk specific gravity of mixtures after 2,6, and 10 min of mechanochemical activation was 1.76± 0.10, 1.72±0.10, and 1.67±0.09 g $cm^{-3}$, respectively.

For the evaluation of degree of transformation of zirconium dioxide in calcium zirconate a batch of 0.6–0.7 g of calcinated mixture of $ZrO_2$ and $CaCO_3$ taken with the accuracy ±0.0001 g was placed in a 50 ml beaker, and 20 ml of 4 M HCl was added. The obtained suspension was stirred with magnetic stirrer at 75–80°C for 2.5 h which provided complete dissolution of calcium zirconate contained in a clinker. Zirconium dioxide does not react with hydrochloric acid under these conditions, which was confirmed by control experiments. Solid residue of $ZrO_2$ was separated by filtration. Procedure of analysis of filtrate is described in [8].

For obtaining of TEM-images JEM-2100F Jeol transmission microscope was used. It was equipped with the built in energodispersion spectrometer of the characteristic X-ray radiation at 200 kV accelerating voltage. Before studies the samples were dispersed in ethanol in the ultrasound bath for 5–10 min.

Specific surface was evaluated by means of low temperature adsorption of nitrogen by means of Flow-Sorb II 2300 (Micromeritics), Values of specific surface of zirconium dioxide in mechanoactivated mixtures before and after calcinations was evaluated after removing of unreacted carbonate and calcium oxide, and also calcium zirconate by dissolution in hydrochloric acid. X-ray photographs were obtained on a Shimadzu XRD-6000 diffractometer (Cu$K_\alpha$-radiation). Scanning was carried out with the step 0.02°, accumulation time 1 s. Thermal analysis was carried out on a NETZSCH STA 409 PC/PG installation. Results were obtained in the regime of heating a sample with the rate 10°C/min in a crucible of aluminum oxide under argon.

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