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Kinetic and Thermodynamic Patterns of $CaZrO_3$ Formation at Sintering Zirconium Dioxide with Calcium Carbonate

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Abstract—Experimental data were obtained on the kinetics of formation of calcium zirconate in the system of ZrO_2–$CaCO_3$ with a 1:1 molar ratio of the components at 1000, 1100, 1200, and 1300ºC. The thermodynamic characteristics of reactions occurring during sintering zirconium dioxide and calcium carbonate were calculated. The changes in specific surface area of zirconium dioxide at heating and its effect on the kinetics of the studied process were investigated. Analysis of experimental data on the degree of $CaZrO_3$ formation was performed using the fundamental equations of the kinetics of solid-state reactions. The best agreement between the calculation and the experiment was obtained for Jander and Zhuravlev–Lesokhin–Tempelman diffusion models.

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Calcium zirconate $CaZrO_3$ plays an important role as an intermediate in the baddeleyite (natural zirconia) technology based on its sintering with calcium carbonate or oxide [1]. The ceramics based on $CaZrO_3$ is a promising material for the elements of the microwave resonant filters and ceramic capacitors [2]. Some published data exist on the degree of formation of calcium zirconate during sintering of ZrO_2 with $CaCO_3$ [3, 4], but no kinetics of this process has been systematically studied. In this paper we report on the study of the kinetic and thermodynamic laws of the formation of $CaZrO_3$ in the system ZrO_2–$CaCO_3$ at a stoichiometric ratio of the components. To study the effect of the state of dispersion of the reagents on the rate of the solid-state reaction we used in the experiments two samples of ZrO_2 differing by the specific surface area: 8.9±0.5 and 0.79±0.05 $m^2 g^{-1}$ They were obtained by calcination of starting reactive grade zirconium dioxide for 12 h at 600 and 1300ºC, respectively. The initial mixture of calcium carbonate and zirconium dioxide samples are further marked as a z-1 and z-2, respectively.

The zirconium dioxide interaction with calcite $ZrO_2 + CaCO_3 = CaZrO_3 + CO_2$ corresponds to the reactions of the type $A_{(s)} + B_{(s)} = C_{(s)} + D_{(g)}$. Experimental study of kinetics of such reactions is convenient in cases when the removal of gas takes place simultaneously with the formation of the solid product, since the degree of conversion can easily be determined by the mass loss of the original mixture. This provides a possibility to minimize the mass of the initial mixture to 100–200 mg, and as a consequence, to reduce the thickness of the reaction layer. By the thermophysical reasons this factor is one of the main conditions for the rapid heating of the whole sample and consequently the correct determination of the beginning of the isothermal process [5]. In practice, the sample with the minimum allowable weight should be put to the oven pre-heated to the T_{iso}, and the total duration of the isothermal keeping is counted from that moment.

As shown below, the studied process first includes dissociation of calcite at heating, and then independently of the first phase CaO reacts with ZrO_2. In this step the mass loss of the sample cannot be used to obtain the experimental kinetic data. To provide the accuracy of the chemical analysis of samples after sintering, we used in our experiments the starting mixtures with the weight of about 1 g. In this case to ensure the validity of the methodology it was necessary to determine: (a) τ^0_{iso}, the time of reaching by the sample of the desired temperature T_{iso}, and (b) the correction $\Delta\tau_{\text{eff}}$, which is the "effective duration of isothermal keeping, which by the yield of the reaction product is equivalent to the initial polythermal heating of the sample" [5]. The total effective duration of isothermal keeping τ_{eff}, which should be used as a time coordinate in the kinetic analysis, is described by the relation (1).

$$\tau_{\text{eff}} = \Delta\tau_{\text{eff}} + \tau_{\text{iso}}. \tag{1}$$

When the sample is placed to a preheated oven, it is difficult to determine $\Delta\tau_{\text{eff}}$ due to a large temperature gradient, uneven heating of the sample, and the difficulty of determining the changes in its temperature over time. This problem is simplified when the heating is carried out gradually. In this paper, the initial mixture in a corundum crucible was placed at room temperature in the center of the oven near the temperature sensor, and the heating started. After reaching the T_{iso} the sample was maintained for a given time, then removed from the oven and cooled to room temperature in a desiccator containing silica gel. The schedule of reaching the isothermal mode was the same for each T_{eff} in different series of experiments that was monitored by constructing the heating time–temperature plots. Compared with the method when the initial mixture is placed in a preheated oven, this approach has the following advantages. Due to the gradual increase in the temperature, the sample heating occurs uniformly, and the reaction begins simultaneously throughout the sample bulk. In addition, at the introduction of the sample in a hot oven its ejection from the crucible by the gaseous products released at the sharp temperature rise is not excluded.

When the heating is carried out gradually it can be assumed that the temperature of the sample in the polythermal step is equal approximately to the temperature in the furnace. The value of $\Delta\tau_{\text{eff}}$ can be calculated by the equation [5]:

$$\tau_{\text{eff}} = \int_{\tau_0}^{\tau^0_{\text{iso}}} \frac{k_\tau}{k_{\text{iso}}}\, d\tau, \tag{2}$$

where the integration is in the range from τ_0 to reaching the isothermal mode τ^0_{iso}, k_{iso} is the reaction rate constant in the isothermal mode ($T = T_{\text{iso}}$); k_τ is the reaction rate constant at temperature T corresponding to the time τ in the polythermal mode. Then, we obtain Eq. (3).

$$k_{\text{iso}} = A\exp\left(-\frac{E_{\text{a}}}{RT_{\text{iso}}}\right),$$

$$k_\tau = A\exp\left(-\frac{E_{\text{a}}}{RT}\right),$$

$$\Delta\tau_{\text{eff}} = \exp\left(\frac{E_{\text{a}}}{RT_{\text{iso}}}\right)\int_{\tau_{\text{o}}}^{\tau^0_{\text{iso}}} \exp\left(-\frac{E_{\text{a}}}{RT}\right)d\tau, \tag{3}$$

where E_{a} is the activation energy, A is the pre-exponential factor.

To calculate $\Delta\tau_{\text{eff}}$ the method of iterations was applied. The integral in Eq. (3) was calculated numerically, for example, by the trapezoids method [6] based on the experimentally established dependence of temperature on the heating time τ in the temperature range from T_0 to T_{iso}. Since at $T < 873$ K the formation of calcium zirconate does not occur (see below), the value of T_0 was taken equal to 873 K.

As a zero approximation $\Delta\tau_{\text{eff}} = 0$ ($\tau_{\text{eff}} = \tau_{\text{iso}}$) was taken and the reaction rate constant was calculated according to the chosen model from the experimental dependence of the degree of reaction completion on the exposure duration at 1000, 1100, 1200, and 1300ºC. The E_{a} value was calculated by linearization of the data obtained in the Arrhenius coordinates. The E_{a} then was substituted into Eq. (3) to determine $\Delta\tau_{\text{eff}}$. With the $\Delta\tau_{\text{eff}}$ value obtained by Eq. (1) we calculated τ_{eff} and the refined values of rate constant, E_{a}, and $\Delta\tau_{\text{eff}}$. The process was repeated until the calculated values of the rate constants, E_{a} and $\Delta\tau_{\text{eff}}$ differed from the previous ones by less than 0.1%. This required no more than four iterations.

According to [4], the only product of the interaction of zirconium dioxide and $CaCO_3$ at a 1:1 molar ratio of reactants is calcium zirconate, and with an excess of ZrO_2 along with the zirconates a solid solution ZrO_2–CaO is formed. It should be noted that $CaZrO_3$, in contrast to the zirconim dioxide and its solid solution with calcium oxide, at processing with heated hydrochloric acid is readily transferred into the solution. This fact was used in this study to measure the degree of completeness of the solid-state reaction. In agreement with the results of [4], in the diffraction patterns of the samples obtained at the sintering (not shown) there are only the peaks of ZrO_2 (baddeleyite), calcium oxide, and $CaZrO_3$. According to X-ray analysis, in the zirconium dioxide after decomposition of the cakes with hydrochloric acid calcium was not

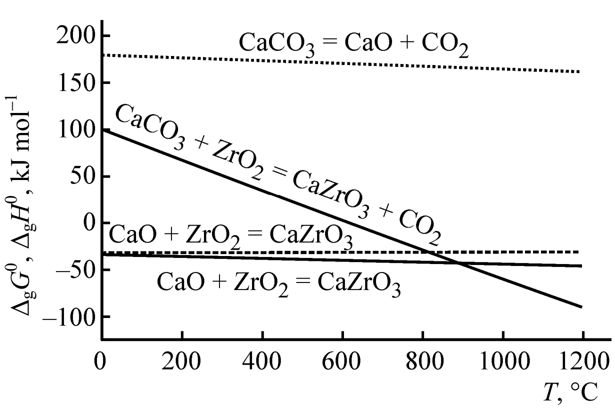

Fig. 1. Temperature dependence of standard Gibbs energies (solid lines) and enthalpies (dashed line) of the reactions of calcium zirconate formation and calcium carbonate decomposition calculated from the data of [7].

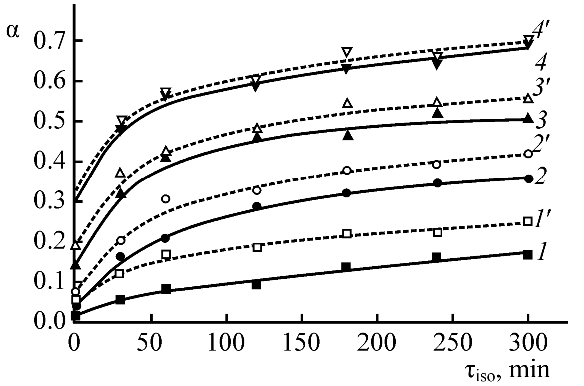

Fig. 2. The experimental degree of conversion (α) as a function of isothermal keeping time (τ_{iso}) in the system of ZrO_2–$CaCO_3$ at the temperatures: (*1, 1'*) 1000°C, (*2, 2'*) 1100°C, (*3, 3'*) 1200°C, (*4, 4'*) 1300°C. Dark symbols and solid lines for mixtures z-2, open symbols and dotted lines for mixtures z-1.

detected, which confirms the conclusions [4] about the lack of ZrO_2–CaO solid solution as a reaction product.

It was shown in [3] that at the sintering ZrO_2 (baddeleyite) with calcium carbonate the formation of $CaZrO_3$ occurred after the $CaCO_3$ decomposition, namely, the process consisted of two steps.

$$CaCO_3 = CaO + CO_2,$$

$$CaO + ZrO_2 = CaZrO_3.$$

Our data of the thermal and chemical analyzes confirm this conclusion. According to the results of thermal analysis of mixtures z-1 and z-2, the weight loss due to thermal decomposition of $CaCO_3$ begins in the range 600–620°C and ends at 880–900°C, with the total weight loss corresponding to the estimated CO_2 content in the mixture. On the DSC curve (not shown) the position of the endo effect maximum at the CO_2 removal (856°C) coincides with the maximum rate of weight loss. It should be noted that on the DSC curve there is no peak corresponding to the formation of $CaZrO_3$. For both mixtures in the polythermal step from room temperature to 900°C the calcium zirconate formation did not exceed 2%.

These experimental results are generally consistent with the thermodynamic calculations performed using the reference data [7] (Fig. 1). The formation of calcium zirconate from calcite and baddeleyite is allowed thermodynamically above 610°C, in conformity with the experimental data [3, 4]. The reaction of $CaZrO_3$ synthesis from CaO and zirconiun dioxide is energetically favorable in the whole investigated temperature range, and its Gibbs energy is weakly dependent on temperature. The formation of calcium zirconate from calcium oxide nd ZrO_2 is exothermic, but the thermal effect by the module is 6 times less than the endo effect of calcite decomposition (Fig. 1). Thus, the lack of appearance of the exo peak of the $CaZrO_3$ formation on the DSC curve can be associated with a relatively small effect and its partial overlapping with the endo peak of $CaCO_3$ dissociation, as well as with a low reaction rate.

At 1205°C the monoclinic zirconium dioxide (baddeleyite) is transformed to tetragonal modification [7] and, strictly speaking, the comparison of the rate constants for the reaction at 1300°C and in the range of 1000–1200°C is incorrect. However, since the enthalpy of the phase transition is small (5.94 kJ mol^{-1} [7]), the Gibbs energy of reaction CaO + ZrO_2 (tetragon.) = $CaZrO_3$ at 1300°C differs from the extrapolated value calculated from the data for the monoclinic modification [7] only by 0.7%. Therefore, in this paper to calculate the activation energy we used the rate constants for all investigated temperatures without the loss of generality of the results.

Figure 2 shows the experimental degree of conversion α as a dependence on the duration of isothermal keeping τ for the mixtures z-1 and z-2. Note that the specific surface area of ZrO_2 in a z-1 mixture is by an order of magnitude greater than in z-2. On this basis it would be expected that the differences in the rate of interaction between the components in these mixtures and as a consequence in the α values should be large at the identical temperature and isothermal keeping time. However, the data in Fig. 2 indicate that

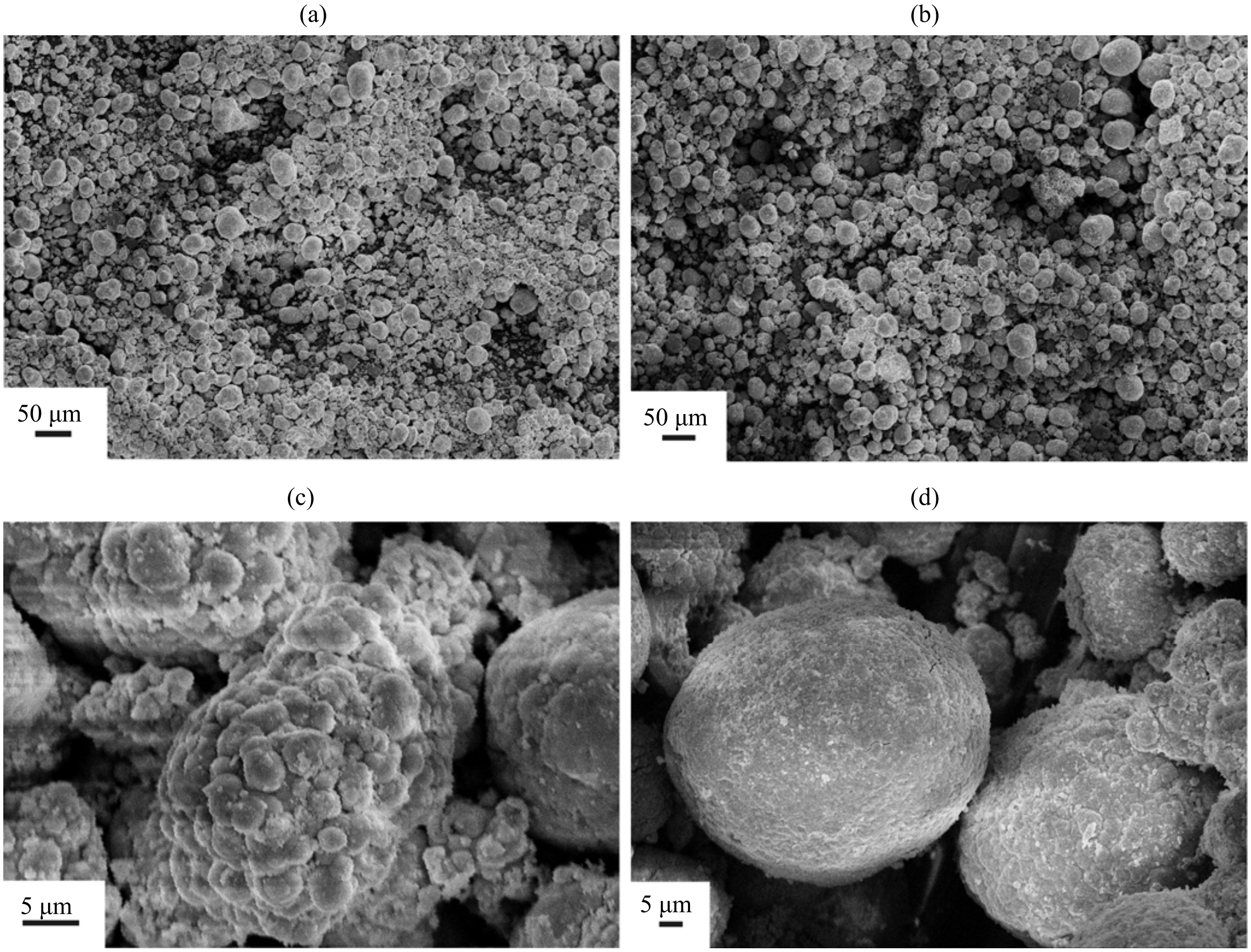

Fig. 3. Scanning electron microscopy images of the initial samples of zirconium dioxide and after sintering at 600°C (a, c) and 1300ºC (b, d): (a, b) 50 μm scale, (c, d) 5 μm scale.

the degree of conversion of the of z-1 mixture is only slightly higher than that of z-2, and with increasing temperature the difference decreases, and at 1300ºC the processes are almost leveled. The apparent contradiction is explained by the peculiarities of the microstructure of the initial ZrO_2 powder and its change during heating.

Figure 3 shows the SEM (scanning electron microscopy) images of the initial samples of zirconium dioxide with specific surface area 9.8±0.5 $m^2 g^{-1}$ (sintered at 600ºC) and 0.79±0.05 $m^2 g^{-1}$ (sintered at 1300ºC). When comparing the images in 50 μ scale it can be seen that the particles of both samples have a round shape and similar size (approximately 10–50 μm), and ZrO_2 particles after sintering at 1300ºC (Fig. 3b) are somewhat larger than those after sintering at 600ºC (Fig. 3a), in agreement with the data on the degree of conversion (Fig. 2). Analysis of the images at higher magnification (5 μm scale) allows us to conclude that the particles of zirconiun dioxide after sintering at 600ºC (Fig. 3c) are aggregates of smaller particles, while sintering at 1300ºC results in their merging and formation of homogeneous dense particles (Fig. 3d). The inner surface of the aggregates (Fig. 3c) is accessible probably to the nitrogen molecules, which explains the significant difference in the $S_{\text{spec.}}$ of two samples of ZrO_2. At the initial stage of the solid-state reaction the outer surface of the aggregates is covered apparently with a layer of product ($CaZrO_3$), and further rate of the process on their inner surface is controlled by the diffusion of the second reagent (CaO) through a layer of calcium zirconate.

In order to elucidate the effect of temperature on specific surface of ZrO_2 as a reagent to be covered, we obtained the plots of $S_{spec.}$ of zirconium dioxide (initial value 8.9±0.5 $m^2\ g^{-1}$) on the isothermal keeping time (Fig. 4). Heating of ZrO_2 was performed as described above for the reaction mixtures. It follows from the data shown in Fig. 4 that at 1000ºC in the polythermal section the specific surface area is reduced by approximately 15% relative to the initial value (9.8 $m^2\ g^{-1}$), and then at the isothermal keeping its gradual reduction occurs by additional ~25%. The sharpest drop in specific surface area of ZrO_2 was observed at the exposure at 1300ºC: at the beginning of the isothermal section the value of $S_{spec.}$ is reduced by an order of magnitude and then remains almost unchanged. The nature of changes in the specific surface area of zirconium dioxide on the time of isothermal keeping (Fig. 4) is consistent with the gradual convergence of curves of the degree of conversion for the z-1 and z-2 mixtures with increasing temperature (Fig. 2).

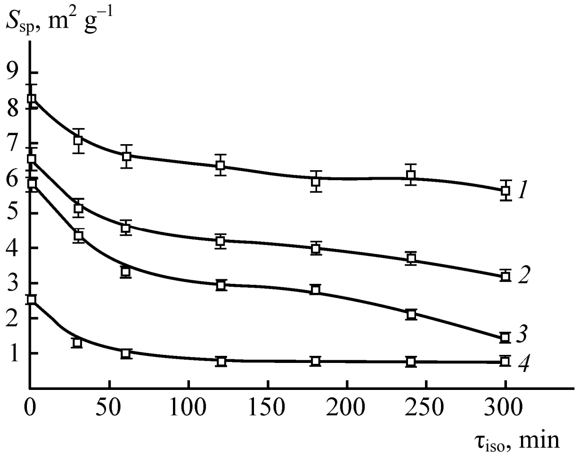

Fig. 4. Changing of the surface area of the initial sample of ZrO_2 pre-calcined for 12 h at 600ºC, depending on the time of isothermal keeping (τ_{iso}) at the temperatures: (*1*) 1000ºC, (*2*) 1100ºC, (*3*) 1200ºC, (*4*) 1300ºC.

To explore a possibility of intensification of the reaction of calcium zirconate formation by increasing the reagents contact surface, we attempted to apply ultrasonic destruction of aggregated particles of ZrO_2 (Fig. 3c). We treated alcoholic suspension of zirconium oxide powder with an initial S_{sp} = 9.8±0.5 $m^2\ g^{-1}$ and a mixture of z-1 using the dispersant UZTA US-0, 1/22-02 "Alena." The duration of the ultrasonic treatment was up to 7 min, the power was varied in the range 75–120 W. After ultrasonic treatment and filtration of suspensions, the powders were dried in air. Further, the ultrasonic-treated mixture z-1 and the stoichiometric mixture of ZrO_2 with $CaCO_3$ treated with ultrasound were sintered by the scheme described above. According to the results obtained, the ultrasonic exposure did not alter the degree of conversion, indicating a sufficient strength of aggregates of particles of zirconium dioxide.

As far as in the case of z-1 mixture the requirement of equal access across the whole surface of the ZrO_2 grains is not ensured, and the surface value varies considerably in the course of the experiment (Fig. 4), for the kinetic analysis were used the data on the degree of conversion obtained for a mixture of z-2 (Fig. 2). The objective of this analysis was to check the adequacy to the experiment of the following models [5, 8, 9]:

(1) The parabolic growth of the product

$$F_{PG}(\alpha) = \alpha^2 = k_{PG}\tau;$$

(2) The contracting sphere

$$F_{CS}(\alpha) = 1 - (1 - \alpha)^{1/3} = k_{CS}\tau;$$

(3) the Avrami–Erofeev model

$$F_{AE}(\alpha) = \ln\,[-\ln(1 - \alpha)] = n\ln\,\tau + \ln\,k_{AE};$$

(4) the Jander model

$$F_{Jander}(\alpha) = [1 - (1 - \alpha)^{1/3}]^2 = k_{Jander}\tau;$$

(5) the model of Zhuravlev–Lesokhin–Tempelman

$$F_{Zh\text{–}L\text{–}T}(\alpha) = \left[\frac{1}{(1 - \alpha)^{1/3}} - 1\right]^2 = k_{Zh\text{–}L\text{–}T}\tau;$$

(6) the Ginstling–Brounstein model

$$F_{GB}(\alpha) = 1 - 2/3\alpha - (1 - \alpha)^{2/3} = k_{GB}\tau.$$

Since the experimental data were obtained for four temperatures, we used a correlation coefficient R_c for the rate constant at each temperature and the accuracy of the straight line of temperature dependence of the calculated rate constants in Arrhenius coordinates, i.e., the correlation coefficient R_c for the activation energy E_a [10], as the criteria for the applicability of a model. Best agreement between calculation and experiment is obtained for the Jander and Zhuravlev–Lesokhin–Tempelman diffusion models. They are well consistent with all the experimental data at 1000ºC and 1100ºC, and at 1200ºC and 1300ºC they correspond to the initial sections of the curves, 0–120 and 0–60 min, respectively. The obtained kinetic parameters were calculated for this set of experimental data. Parameters of the models presented in Table 1 were obtained by

Table 1. Kinetic parameters of the $CaZrO_3$ formation calculated using various models by linearization the data of $F(\alpha)$–τ or $F(\alpha)$–ln τ (for Avrami–Erofeev model)

Model	T, °C	R_c for k	E_a, kJ mol^{-1}	R_c for E_a
Parabolic grow of the product	1000	0.9870	217±5	–0.9995
	1100	0.9739		
	1200	0.9625		
	1300	0.9805		
Contracted sphere	1000	0.9658	161±11	–0.9953
	1100	0.9232		
	1200	0.9168		
	1300	0.9329		
Avrami–Erofeev	1000	0.9932	172±15	–0.9930
	1100	0.9813		
	1200	0.9813		
	1300	0.9999		
Jander	1000	0.9864	239±4	–0.9997
	1100	0.9814		
	1200	0.9747		
	1300	0.9936		
Zhuravlev–Lesokhin–Tempelman	1000	0.9856	264±3	–0.9998
	1100	0.9873		
	1200	0.9843		
	1300	0.9991		
Ginstling–Brounstein	1000	0.9867	231±5	–0.9996
	1100	0.9790		
	1200	0.9709		
	1300	0.9900		

linearization of the data in the coordinates of $F(\alpha)$–τ or $F(\alpha)$–ln τ (for Avrami–Erofeev model). The calculation of rate constants was carried out by the above described scheme using the iterative determination of $\Delta\tau_{\text{eff}}$. The Avrami–Erofeev model is not suitable for this reaction, since the results of computing the parameter n, which in the physical sense must be an integer, takes values from 0.42 to 0.62.

The method of linearization of the data in the $F(\alpha)$–τ coordinates based on the linear method of least squares is often used to calculate the rate constants of reactions and is convenient to compare the adequacy of various kinetic equations, including those for which the degree of conversion cannot be represented in analytical form as a function $\alpha = f(k, \tau)$. However, this method is based on minimizing the sum of squared deviations $\Sigma[F(\alpha^{\text{exp}})–F(\alpha^{\text{calc}})]^2$ and is not the best in terms of minimizing the deviation of the experimental and calculated values of α. If α is represented as a function of τ in analytical form, as, e.g., in the Jander and Zhuravlev–Lesokhin–Tempelman models (4), it is preferable to calculate the rate constants by minimizing the sum $\Sigma(\alpha^{\text{exp}}–\alpha^{\text{calc}})^2$, based on nonlinear least squares [11].

$$\alpha = 1 - (1 - \sqrt{k_{\text{Jander}}\tau})^3$$

$$\alpha = 1 - \frac{1}{(\sqrt{k_{\text{Zh–L–T}}\tau} + 1)^3}. \quad (4)$$

In particular, the standard deviations of values of α, calculated by the Jander model from the experimental values using the method of linearization and nonlinear least squares for 1000, 1100, 1200 and 1300ºC in the first case is higher than in the second one by 6, 24, 36, and 26%, respectively.

Table 2 shows the kinetic parameters calculated for the Jander and Zhuravlev–Lesokhin–Tempelman models based on the minimization of the sum $\Sigma(\alpha^{\text{exp}}–\alpha^{\text{calc}})^2$ using nonlinear least squares according to the above iteration scheme. The errors in Tables 1 and 2 are the mean square deviations.

Figure 5 shows the experimental degree of conversion α in the generalized coordinates $\tau_{\text{eff}}/\tau_{\text{eff}}^{1/3}$, where $\tau_{\text{eff}}^{1/3}$ is the time at which the degree of conversion $\alpha = 1/3$. In this case, the data for different temperatures can be represented as a one curve of the shape typical for the solid-phase reaction rate-limiting step (diffusion through the reaction product, chemical transformation at the interface, nucleation of new phases) [8]. The data shown in Fig. 5 confirm that the formation of $CaZrO_3$ during sintering of zirconium dioxide and calcium carbonate is controlled by diffusion.

EXPERIMENTAL

In the experiments a monoclinic zirconium dioxide (baddeleyite) of the reagent grade and calcium carbonate (calcite) of analytical grade were used. According to X-ray analysis, the content of HfO_2 with respect to the sum of (ZrO_2+HfO_2) in the sample of zirconium dioxide was 0.11 wt %. Calcium carbonate was dried at 110ºC for 24 h.

The initial mixtures containing ZrO_2 and $CaCO_3$ at the molar ratio of 1:1 were prepared by joint process-

Table 2. Kinetic parameters of the $CaZrO_3$ formation calculated with the models of Jander [Eq. (1)] and Zhuravlev–Lesokhin–Tempelman [Eq. (2)] by the minimization of the sum $\Sigma\,(\alpha^{exp}-\alpha^{calc})^2$ using nonlinear least squares

Model	T, °C	k, min^{-1}	R_k for k	$\Delta\tau_{eff}$, min	E_a, kJ mol^{-1}	R_k for E_a
1	1000	$(1.13\pm0.07)\times10^{-5}$	0.9910	4.33	251±8	–0.9990
	1100	$(7.40\pm0.46)\times10^{-5}$	0.9903	5.34		
	1200	$(3.26\pm0.27)\times10^{-4}$	0.9918	6.95		
	1300	$(1.03\pm0.13)\times10^{-3}$	0.9876	7.21		
2	1000	$(1.24\pm0.08)\times10^{-5}$	0.9899	4.21	273±7	–0.9993
	1100	$(9.56\pm0.54)\times10^{-5}$	0.9938	5.16		
	1200	$(4.64\pm0.31)\times10^{-4}$	0.9964	6.70		
	1300	$(1.71\pm0.14)\times10^{-3}$	0.9966	6.92		

sing of calculated batches of reagents in a mechanical mortar Fritsch Pulverisette 2 in the mode of mixing, that is, with minimal clamping pestle to the mortar, for 4 h. The degree of homogeneity of the mixture was monitored by the constancy of content of volatile component (CO_2) in it and its correspondence to the calculated value. The CO_2 content was determined on the basis of weight loss at the parallel calcination of four samples at 1000ºC for 3 h. Bulk density of the z-1 and z-2 mixtures amounted to 1.52±0.08 and 1.75±0.10 g cm^{-3}, respectively.

The sintering of zirconium dioxide mixtures with calcium carbonate was carried out at the temperatures 1000, 1100, 1200 and 1300ºC in an electric oven SNOL 6,7/1300 in air. Each point was determined from the results of 2–3 parallel experiments. After sintering, the samples were stored in a desiccator till the analysis.

To determine the degree of conversion (α) of zirconium dioxide in calcium zirconate, a weighed porion of 0.6–0.7 g of a mixture of calcined ZrO_2 and $CaCO_3$, taken with an accuracy of ±0.0001 g, was placed in a 50 ml beaker and 20 ml of 4M HCl was poured to it. The resulting suspension was stirred with a magnetic stirrer with heating at 75–80°C for 2.5 h, which ensured complete dissolution of calcium zirconate contained in the sample. Zirconium dioxide does not react with hydrochloric acid under these conditions, which was confirmed by control experiments. The solid residue (ZrO_2) was separated by filtration through "blue ribbon" filter paper. If necessary, the filtration was repeated 2–3 times to eliminate the breakthrough. The concentration of zirconium in the filtrate was determined photometrically by the method based on the interaction of zirconium with arsenazo I reagent, as in [12]. The value of α was calculated as the ratio of amounts of zirconium in the solution and in the original sample. The accuracy of the analysis was controlled by the mass balance of zirconium, which passed into a solution from the cake, and remaining on the filter in the form of undecomposed ZrO_2. The relative error of the degree of conversion was estimated at 10%.

The specific surface area was determined by low-temperature nitrogen adsorption on a Flow–Sorb II 2300 (Micromeritics) analyzer. To obtain images by scanning electron microscopy (SEM) a LEO–1450 microscope was used. X-ray analysis was performed on a DRON-2 instrument (CuKα radiation), registration rate 2°(2θ)/min. Thermal analysis was performed on a NETZSCH STA 409 PC/PG installation. The results were obtained at heating the sample at a rate of 10ºC/min in the crucible of aluminum oxide in an

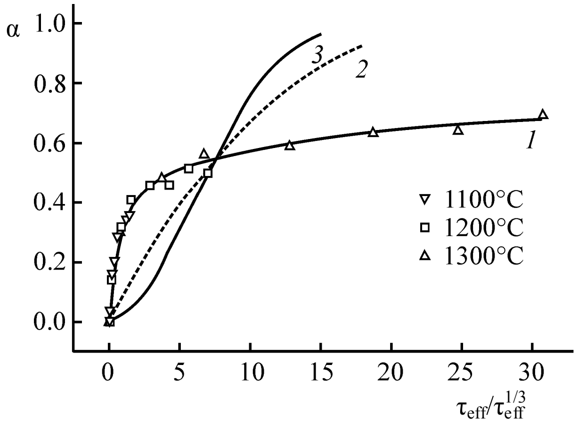

Fig. 5. The experimental degree of conversion (α) in generalized coordinates and the kinetic curves describing: (*1*) diffusion through the reaction product, (*2*) chemical conversion at the interface, (*3*) nucleation of a new phase.

argon atmosphere. The X-ray spectral analysis was performed using a spectrometer Spectroscan MAX-GV.

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