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Influence of Mechanical Activation on the Kinetic Features of $SrZrO_3$ Formation

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Abstract—Strontium zirconate $SrZrO_3$ has been synthesized via heating of equimolar mixture of $SrCO_3$ and ZrO_2 at 900–1050°C with and without preliminary mechanical activation of the reactants. Data on the degree of $SrZrO_3$ formation have been analyzed using the basic equations of the kinetics of solid-state reactions. The best agreement of the theoretical prediction with the experimental results has been obtained in the case of the Zhuravlev–Lesokhin–Tempelman equation. Mechanical activation of the $SrCO_3$–ZrO_2 mixture for 2–10-min causes marked acceleration of $SrZrO_3$ formation in the course of subsequent sintering.

Keywords: strontium zirconate, synthesis, mechanical activation, kinetics

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Alkaline-earth metal zirconates (in particular, strontium zirconate $SrZrO_3$) are promising materials for development of capacitors, catalysts, and high-temperature thermal insulators as well as for other applications [1–3]. Formation of strontium zirconate via reaction (1) has been studied in [4–6] in view of synthesizing the ceramics, but kinetic features of the synthesis have received only limited attention. For reaction (1) to be complete, a mixture of the reactants should be heated during several hours at fairly high (1200°C or above) temperature [4–6].

$$SrCO_3 + ZrO_2 = SrZrO_3 + CO_2. \quad (1)$$

A possible way to intensify a solid-state reaction is mechanical activation [7–10]. We have examined kinetics of $CaZrO_3$ synthesis by sintering a $CaCO_3$–ZrO_2 mixture without [11] and with [12] mechanical activation, and have obtained the best agreement between the predicted parameters and the experimental results when using the Jander and the Zhuravlev–Lesokhin–Tempelman equations. Mechanical treatment of the reactants in a centrifugal planetary mill significantly accelerates the synthesis of calcium zirconate in the course of subsequent sintering [12]. It has been found that preliminary mechanical activation of ZrO_2 and $SrCO_3$ allows decreasing the $SrZrO_3$ formation temperature, but no kinetic study of the $SrZrO_3$ synthesis has been performed [13].

Herein we report on kinetic features of $SrZrO_3$ formation via sintering an equimolar mixture of zirconia and strontium carbonate with and without mechanical activation of the reactants as compared to the analogous synthesis of calcium zirconate.

Both with and without mechanical activation of a $CaCO_3$–ZrO_2 mixture, $CaZrO_3$ formation occurred after complete thermolysis of calcium carbonate [11, 12], i.e., the synthesis actually proceeded according to Eq. (2):

$$CaO + ZrO_2 = CaZrO_3. \quad (2)$$

As shown by high-temperature X-ray diffraction analysis, the intermediates of the studied reaction were solid solutions based on tetragonal and cubic ZrO_2 modifications [6]. Thermal analysis indicated that individual strontium carbonate was more stable than its calcium analog: $SrCO_3$ underwent decomposition at 1050–1200°C, far above the $CaCO_3$ decomposition temperature range (300–400°C) [4, 5]. The obtained thermal analysis data were consistent with the temperature dependence of the standard Gibbs energy $\Delta_r G^0$ calculated in [14] for the $CaCO_3$ and $SrCO_3$ decomposition reactions (Fig. 1). Thermodynamic calculation showed that calcium carbonate and strontium carbonate became unstable at above 880°C and 1140°C, respectively. Figure 1 also presents the temperature dependence of $\Delta_r G^0$ for the reactions of

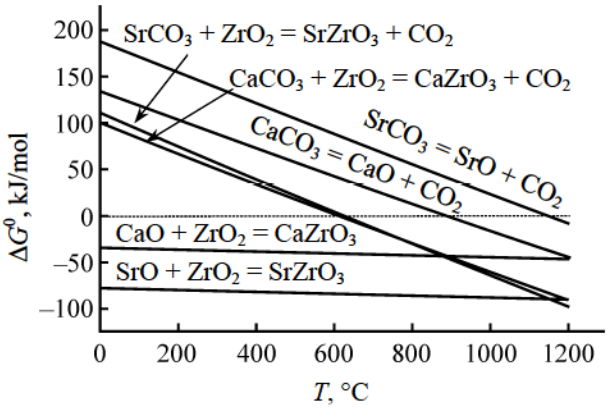

Fig. 1. Gibbs energy of the $CaZrO_3$ and $SrZrO_3$ formation reactions and of the $CaCO_3$ and $SrCO_3$ decomposition reactions (according to [14]).

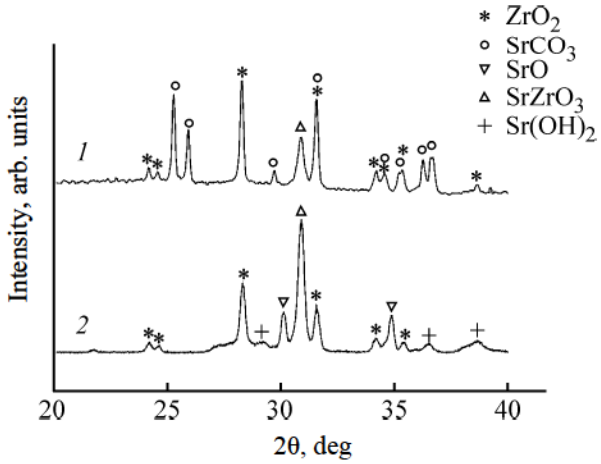

Fig. 2. X-ray diffraction patterns of the $SrCO_3$–ZrO_2 mixture sintered for (*1*) 3 h at 900°C and (*2*) 4 h at 1050°C.

$CaZrO_3$ and $SrZrO_3$ formation from calcium or strontium oxide/carbonate and zirconia. The reactions of $CaZrO_3$ and $SrZrO_3$ formation from the corresponding carbonates and ZrO_2 were thermodynamically allowed $T > 620$°C (Fig. 1). However, synthesis of calcium zirconate by heating a $CaCO_3$–ZrO_2 mixture without preliminary mechanical activation proceeded with significant rate only above 900–1000°C, after complete decomposition of calcium carbonate, according to Eq. (2) [6, 11]. Reaction (2) was energetically favorable over a wide temperature range, with the Gibbs free energy varying from –78 to –90 kJ/mol at 0–1200°C range (Fig. 1).

According to published data, the reaction of $SrZrO_3$ synthesis via sintering a $SrCO_3$–ZrO_2 mixture has about 200°C lower onset temperature [6] and proceeds more vigorously than the similar reaction of $CaZrO_3$ synthesis [4]. High-temperature X-ray diffraction analysis showed that the synthesis of strontium zirconate by heating an equimolar mixture of $SrCO_3$ and ZrO_2 proceeded according to Eq. (1) with formation of an intermediate solid solution based on the cubic modification of ZrO_2; the SrO phase was not detected [6].

Figure 2 presents X-ray diffraction patterns of the initial mixture of zirconia and strontium carbonate that was sintered during 3 h at 900°C or 4 h at 1050°C without mechanical activation. The sample obtained via sintering at 900°C contained the reactants and $SrZrO_3$ (Fig. 2, curve *1*), corresponding to formation of strontium zirconate via reaction (1). In the X-ray diffraction pattern of the sample sintered at 1050°C (Fig. 2, curve *2*), peaks of $SrCO_3$ disappeared, and reflections from strontium oxide and hydroxide appeared (strontium hydroxide was formed the via the reaction of SrO with atmospheric moisture). Obviously, the decomposition temperature of $SrCO_3$ decreased in the presence of ZrO_2, and at 1050°C $SrZrO_3$ was formed primarily via the reaction between strontium oxide and zirconia:

$$SrO + ZrO_2 = SrZrO_3. \quad (3)$$

In [6], high-temperature X-ray diffraction analysis was performed to elucidate composition of the samples obtained at 980°C (other samples prepared at 900–1200°C were not characterized with X-ray diffraction). Noteworthily, the reflections from strontium oxide having a cubic lattice and those from the cubic modification of ZrO_2 were very close. That was apparently the reason why strontium oxide phase was not detected during $SrZrO_3$ formation via sintering a zirconia–strontium carbonate mixture [6].

Results of thermodynamic calculations (Fig. 1) were consistent with the experimentally established fact that the reaction of $SrZrO_3$ synthesis via heating a $SrCO_3$–ZrO_2 mixture was faster than the similar reaction of $CaZrO_3$ synthesis in the 900–1200°C range [4]. Indeed, at $T > 900$°C both the possible $SrZrO_3$ synthesis reactions [Eqs. (1) and (3)] were energetically advantageous over the $CaZrO_3$ synthesis reaction according to Eq. (2).

Thus, the synthesis of $SrZrO_3$ via sintering a $SrCO_3$–ZrO_2 mixture at 900–1200°C revealed a more complex character than that of the analogous synthesis of $CaZrO_3$. First, strontium zirconate was formed both via reactions (1) and (3), whereas formation of calcium

zirconate was preceded by complete decomposition of $CaCO_3$. Second, in the 920–950°C range, a polymorphic transformation from orthorhombic to hexagonal $SrCO_3$ occurred [4–6]. Hence, the reactivity of strontium carbonate should have been increased due to the Hedvall effect; correspondingly, the synthesis reaction should have been accelerated at that temperature range. Moreover, comparison of the Tammann temperatures of the reactants, taking into account the size of the alkaline-earth metal ions, suggested that formation of $CaZrO_3$ proceeded via the unidirectional diffusion of calcium ions into zirconia [6], whereas $SrZrO_3$ was apparently formed via the mutual diffusion.

The above-mentioned factors complicated kinetic analysis of the $SrZrO_3$ synthesis; in that case, contrary to the $CaZrO_3$ synthesis [11, 12], a rigorous quantitative description in terms of a single kinetic model was problematic. Indeed, the reaction type changed in the course of the reactants heating to the temperature at which formation of $SrZrO_3$ proceeded at a sufficient rate ($T > 900$°C). The temperature ranges of reactions (1) and (3) occurrence were not clearly differentiated. Therefore, mathematical processing of the kinetic data, as presented below, was primarily phenomenological in character, and the calculated rate constants should be regarded as effective parameters that are not necessarily strictly related to the mechanism of the processes involved.

Data markers in Fig. 3 show experimental kinetics of formation degree of $SrZrO_3$ (expressed as fraction of unity) in the course of the $SrCO_3$–ZrO_2 mixture heating without mechanical activation at 900, 950, and 1050°C. Kinetic analysis consisted in fitting of the experimental data with the model of parabolic rate law for the product formation, the contracting sphere model, and the models based on the Avrami–Erofeev, Jander, Ginstling–Brounshtein, and Zhuravlev–Lesokhin–Tempelman equations [15]. The best agreement between the calculated and the experimental values was obtained with the Zhuravlev–Lesokhin–Tempelman diffusion model [Eq. (4)]:

$$\{[1/(1-\alpha)^{1/3}] - 1\}^2 = k\tau, \quad (4)$$

where α, the degree of $SrZrO_3$ formation; τ, time of isothermal holding; and k, the reaction rate constant.

The Table lists the rate constants k [calculated by minimizing the $\Sigma(\alpha^{exp}-\alpha^{calc})^2$ sum taking advantage of the nonlinear least-squares method] and the corresponding correlation coefficients R. The fit accuracy is expressed as mean-square deviation.

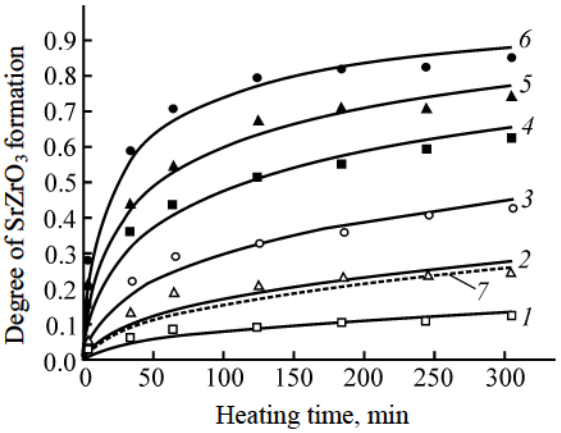

Fig. 3. (Markers) Experimental and (lines) calculated degree of $SrZrO_3$ formation during heating of the $SrCO_3$–ZrO_2 mixture (*1–3*) without mechanical activation and (*4–6*) with mechanochemical activation. The activation time (*4*) 2 min, (*5*) 6 min, and (*6*) 10 min. Sintering temperature (*1*) 900°C, (*2*) 950°C, (*3*) 1050°C, and (*4–6*) 1000°C. (*7*) degree of $CaZrO_3$ formation during heating the $CaCO_3$–ZrO_2 mixture at 1050°C without mechanical activation [11].

According to the X-ray diffraction data (not presented here), mechanical activation of the $SrCO_3$–ZrO_2 mixture resulted in a marked weakening and broadening of peaks in the X-ray diffraction patterns, indicative of a decreased size of the microcrystallites and of somewhat defective structure. Coinciding with the thermodynamic data (Fig. 1), reflections of $SrZrO_3$ and other new phases were not detected in the X-ray diffraction patterns of the mechanically activated mixtures. Chemical analysis showed that vigorous mechanical milling caused only negligible interaction of the reactants via reaction (1): The degree of $SrZrO_3$ formation after 2, 6, and 10 min of mechanical activation was of 0.9, 1.2, and 1.4%, respectively. The experimental $\alpha(SrZrO_3)$ data for the mechanically activated mixtures sintered at 900, 950, and 1000°C (subtracted for the $SrZrO_3$ fraction formed during mechanical activation) are presented in Figs. 4, 5, and 3, respectively. Similarly to the case of calcium zirconate formation [12], the experimental data were most adequately described with the Zhuravlev–Lesokhin–Tempelman model. The calculated rate constants are listed in the table.

To conclude, preliminary mechanical activation of the mixture of the reactants for up to 10 min led to a 2–3-fold increase in the degree of $SrZrO_3$ formation (Figs. 3–5). Mechanical activation of the mixture for 2–10 min increased the process rate constant by

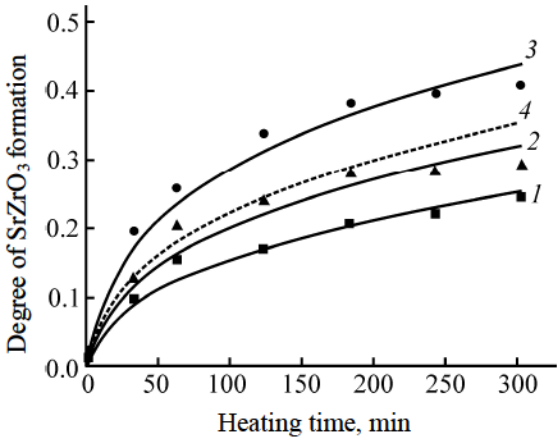

Fig. 4. (Markers) Experimental and (lines) calculated degree of $SrZrO_3$ formation during heating the mechanically activated $SrCO_3$–ZrO_2 mixture at 900°C. Time of mechanical activation: (*1*) 2, (*2*) 6, and (*3*) 10 min. (*4*) degree of $CaZrO_3$ formation during heating the $CaCO_3$–ZrO_2 mixture at 900°C after mechanical activation during 10 min [12].

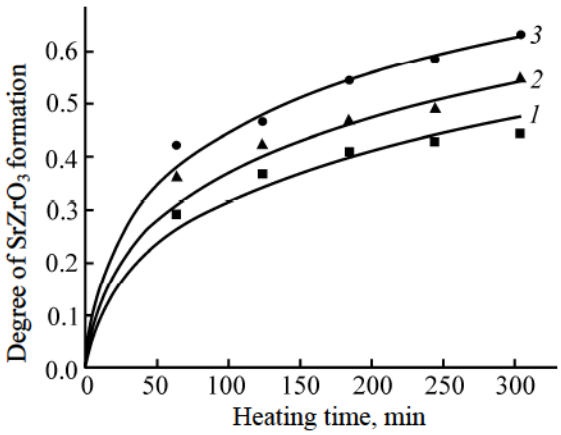

Fig. 5. (Markers) Experimental and (lines) calculated degree of $SrZrO_3$ formation during heating the mechanically activated $SrCO_3$–ZrO_2 mixture at 950°C. Time of mechanical activation: (*1*) 2, (*2*) 6, and (*3*) 10 min.

4–20 times (see the table). $SrZrO_3$ synthesis was complete after mechanical activation of the $SrCO_3$–ZrO_2 mixture during 10–15 min followed by sintering at 1050–1100°C during 3–5 h. Degree of $CaZrO_3$ formation via heating of an equimolar mixture of $CaCO_3$ and ZrO_2 at 1050°C without mechanical activation and via heating at 900°C after 10 min of mechanical activation [11, 12] is shown in Figs. 3 and 4 for comparison. The $SrCO_3$–ZrO_2 and $CaCO_3$–ZrO_2 mixtures were prepared using the identical zirconia sample; the experiments were run under identical conditions. In the case of the inactivated mixtures, the degree of formation of $SrZrO_3$ after certain sintering time exceeded that of $CaZrO_3$ nearly twofold (Fig. 3). In the case of the mechanically activated mixtures, the difference was less significant (Fig. 4). Preliminary mechanical activation of the reactants in the centrifugal planetary mill allowed decreasing the synthesis temperature by 200–250°C for $CaZrO_3$ [11, 12] and by 100–150°C for $SrZrO_3$. Hence, mechanical activation is more efficient in accelerating synthesis of calcium zirconate as compared to the strontium analog.

$SrZrO_3$ formation rate constants k calculated via the Zhuravlev–Lesokhin–Tempelman equation (R is correlation coefficient)

Time of mechanical activation, min	T, °C	k, min^{-1}	R
0	900	$(8.06\pm0.94) \times 10^{-6}$	0.9506
	950	$(4.30\pm0.52) \times 10^{-5}$	0.9592
	1050	$(1.62\pm0.19) \times 10^{-4}$	0.9673
2	900	$(3.48\pm0.23) \times 10^{-5}$	0.9895
	950	$(1.88\pm0.11) \times 10^{-4}$	0.9938
	1000	$(5.88\pm0.37) \times 10^{-4}$	0.9946
6	900	$(6.32\pm0.55) \times 10^{-5}$	0.9835
	950	$(2.90\pm0.18) \times 10^{-4}$	0.9930
	1000	$(1.31\pm0.08) \times 10^{-3}$	0.9963
10	900	$(1.48\pm0.10) \times 10^{-4}$	0.9913
	950	$(4.97\pm0.30) \times 10^{-4}$	0.9952
	1000	$(3.34\pm0.20) \times 10^{-3}$	0.9980

EXPERIMENTAL

Monoclinic zirconia ("chemical pure" grade) and strontium carbonate ("analytical pure" grade) with the specific surface areas of 0.74 and 2.59 m^2/g, respectively, were used in the experiments. The initial mixture containing ZrO_2 and $SrCO_3$ in the 1 : 1 mol/mol ratio was prepared by mixing the weighted portions of the reactants in a Fritsch Pulverisette 2 mortar grinder during 4 h. Mechanical activation of the $SrCO_3$–ZrO_2 mixture was performed in an AGO-2 laboratory centrifugal planetary mill [8] at centrifugal factor of 40*g*. To do so, steel balls of 8 mm in diameter (200 g) and the sample (10 g) were loaded into the gringing vial. Every two minutes the mill was stopped, and the load was stirred. The contamination introduced by the finely dispersed iron material of the grinder was minimized by preliminary lining of the drums and balls as described in [16]. Our previous study of $CaZrO_3$

synthesis from calcium carbonate and zirconia revealed that the mechanical activation of the mixed initial substances was more efficient (in terms of the product yield at subsequent sintering) than their separate mechanical activation followed by mixing the reactants [12]. Therefore, in this study we also carried out combined mechanical activation of ZrO_2 and $SrCO_3$. The specific surface areas of the $SrCO_3$–ZrO_2 mixtures after 2, 6, and 10 min of mechanical activetion were of 4.4, 7.1, and 8.9 m^2/g, respectively.

The resulting mixtures were heated in air in an SNOL 6.7/1300 electric furnace as described in [11]. Each experiment was performed in duplicate or in triplicate to ensure reproducibility. A sample (0.9–1.0 g) was placed in a corundum crucible (6–7 g) and was heated in an oven starting from room temperature. After reaching the desired temperature, the samples were held for a predetermined time, removed from the oven, and cooled in a desiccator over silica gel. The pre-isothermal heating stage was accounted for (along with the experimental kinetic data) to determine the $\Delta\tau_{eff}$ parameter. The latter is the time of isothermal holding equivalent to the pre-isothermal heating of the sample in terms of the degree of formation of the synthesis product [11]. For temperatures of 900–1050°C, $\Delta\tau_{eff}$ ranged from 3 to 6 min.

The degree of conversion of zirconia into strontium zirconate α was determined as follows. 9 M HCl solution (30 mL) was poured into the 0.6–0.7 g precisely weighed specimen of the sintered mixture. The resulting suspension was stirred with a magnetic stirrer at 80–85°C for 3 h, till complete dissolution of strontium zirconate contained in the sinter. Under those conditions zirconia did not react with hydrochloric acid, as confirmed by reference experiments. The resulting solid residue was removed by filtration; and the filtrate was analyzed as described elsewhere [11]. The parameter α was estimated from the weight of the solid residue (ZrO_2), the amount of zirconium in the filtrate, and the weight loss during the mixture sintering.

X-ray diffraction analysis was performed using a Shimadzu XRD 6000 diffractometer (CuK_α radiation) at the scanning speed of 2 deg/min. The specific surface area was determined by low-temperature nitrogen adsorption using a Flow-SorbII 2300 (Micromeritics) analyzer.

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