Solid-Phase Transformations of Monoclinic Zirconium Oxide under Mechanical Treatment in the Devices of Different Types

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Abstract

The effect of mechanical activation of well crystallized zirconium oxide of monoclinic modification in a centrifugal planetary activator mill and in vibratory mill on the characteristics of fine crystalline structure and phase transformation depending on the treatment environment and mechanical loading is investigated. It is established that the mechanical action in the centrifugal planetary mill stimulates dispersion processes, accumulation of microdeformations, and phase transition of the oxide into the tetragonal form. The rate of processes depends on the environment of treatment: for mechanical activation of the dry powder, the phase transition occurs within 15 min, the rate of the process decreases in the presence of water as additive. Treatment in vibratory mill causes mainly crushing of the particles and accumulation of microdeformations. After 2 h, the size of crystallites decreases to 38 nm and remains unchanged during further treatment; gradual accumulation of microdeformations and amorphization of structure occur. After 15 h, the fraction of the crystalline phase was 15 %; no formation of other crystalline phases was observed. The formation of a metastable tetragonal form of ZrO_2 in the activator apparatus can be due to the pulsed character of powerful mechanical action, which causes intense crushing of the crystallites (≥ 20 nm) and can create local conditions favourable thermodynamically and kinetically for the phase transition in separate regions of the solid.

INTRODUCTION

At present, the advanced areas of technology widely use the materials based on different polymorphous forms of zirconium oxide, due to their high thermal stability, mechanical strength and unique surface characteristics. Of special interest are high-temperature modifications of ZrO_2, which are efficiently used to obtain construction and ion exchange materials, selective adsorbents, components of heterogeneous catalysts. Catalytic systems containing tetragonal ZrO_2 promoted with sulphate anions or the anions of heteropolyacids, and other additives, catalyze many chemical reactions. For instance, the skeletal isomerization of n-alkanes proceeds at relatively low temperature (below 250 °C) with a high yield of strongly branched isomers having increased octane characteristics [1].

Several approaches to the synthesis of metastable high-temperature zirconium oxides are known. Widespread are methods of synthesis of the tetragonal and cubic ZrO_2 forms at high temperature (above 1200 °C), which is thermodynamically favourable for the reaction to proceed [2, 3]. By means of rapid quenching of the product, one succeeds in conserving the high-temperature phases in the metastable state. They can also be obtained by means of explosion under which high temperature and pressure are developed [3, 4]. For the catalyst preparation, the most widely spread method is that based on the deposition

of fine hydroxide precursors from which the oxide phase of tetragonal or cubic modification is formed by lengthy thermal activation (at a temperature within 500−700 °C) [1, 5]. For any of the indicated methods, stabilization of the high-temperature forms is promoted by polyvalent metal cations as additives: Y^{3+}, Fe^{3+}, Mn^{2+}, Ca^{2+} and/or anions SO_4^{2-}, WO_4^{2-}, MoO_4^{2-}. According to [5−7], the introduction of the listed additives slows down the crystallization of ZrO_2 at temperatures below 500−700 °C. For the nanosized crystallites, from the thermodynamic point of view, the high-temperature modifications turn out to be more favourable than the monoclinic form [7, 8], because of lower surface energy (770 erg/cm^2 for the tetragonal form [9] against 1130 erg/cm^2 for the monoclinic form [8]). The critical crystallite size for which the existence of the particles of tetragonal form becomes possible at room temperature is 30 nm [7, 8]. According to the data reported in [10, 11], tetragonal ZrO_2 can be obtained from the monoclinic form by means of grinding in a mill for a long time. After grinding in a ball mill for 50 h, the yield of this form was about 45 % and the crystallite size did not exceed 10 nm [10]. Under grinding in Pulverizette mill in the presence of α-Fe_2O_3 as additive, monoclinic ZrO_2 was transformed into the cubic modification almost completely after 60 h [11]. The authors of [12] obtained the tetragonal form of ZrO_2 by means of the soft mechanochemical synthesis followed by calcination of the product at rather low temperature (450 °C).

Advance in the development of experimental equipment and methods for mechanical activation opened new possibilities for enhancement of the reactivity of solids, stimulation of solid-phase chemical reactions and development, on this basis, of new reagent-free procedures for obtaining fine dispersed materials in metastable state [13]. During mechanical treatment in high-energy devices like centrifugal planetary mill, the conditions are realized not only for efficient crushing of the particles. For high rate of powerful mechanical pulse input, local high temperature and pressure can be created in separate sites of a solid (mainly at the sites of contact with the milling bodies during collisions),

and substantial shear strain can arise, which causes plastic yielding and is favourable for the process kinetics. We have shown recently [14] that the nanostructured ZrO_2 of the tetragonal modification can be obtained within several minutes from the fine dispersed amorphous zirconium hydroxide and also from the well crystallized oxide of the stable monoclinic modification by treating in high energy strain mechanochemical device like a centrifugal planetary mill.

The goal of the present work is to investigate the solid-phase transformations of crystalline zirconium oxide of the monoclinic modification depending on the type of grinding device, conditions and mechanical loading.

EXPERIMENTAL

Well-crystallized zirconium oxide of the monoclinic modification, reagent grade «ch.» (pure) was used for mechanical treatment. The process was carried out in a vibratory mill KM-1 with agate balls and in the activator mill AGO-2 of centrifugal-planetary type with two hermetic steel cylinders with a volume of 150 ml each. The cylinder rotation frequency in AGO-2 activator was 1820 rpm, which corresponded to the milling bodies acceleration of 600 m/s^2, that is, 60g. Steel balls 3 mm in diameter, with the total mass of 106 g, and 3 g of zirconium oxide were charged into a cylinder. For the humid activation regime, 3 ml of distilled water was added into the cylinder. While in operation, the cylinders of AGO-2 were cooled with water in order to exclude substantial heating of the material under treatment. The mechanical loading was varied by changing treatment duration from 30 s to 30 min in AGO-2 and up to 15 h in KM-1 apparatus.

The X-ray diffraction patterns of the products of treatment were recorded with DRON-3 diffractometer by scanning over points using filtered CuK_α radiation. Scanning was performed with a step of 0.02 deg (30−50 points per peak); accumulation time was 1 s. The approximating Foigt's function, a convolution of Cauchy and Gauss functions, was used for the analytical description of the diffraction

reflections [15, 16]. Separation of the contributions into broadening due to the crystallite size and due to defects was carried out according to Williamson – Hall procedure [17, 18].

RESULTS AND DISCUSSION

The diffraction patterns of the products formed under treatment of the dry zirconium oxide powder in a vibratory mill depending on mechanical loading are shown in Fig. 1. Gradual decrease in the intensity and broadening of the diffraction lines of the initial phase are observed with an increase in the duration of treatment. After 15 h, mean crystallinity degree calculated from the ratio of intensities of the main diffraction peaks before and after treatment $((I_{mech}/I_{init}) \times 100~\%)$ was only 15 % (Fig. 2). No formation of new crystalline phases was observed.

Under treatment in activator mill, as early as after 30 s a weak broadened reflection 111 ($d = 2.96$) of the new phase of tetragonal ZrO_2 is registered in the diffraction patterns (Fig. 3),

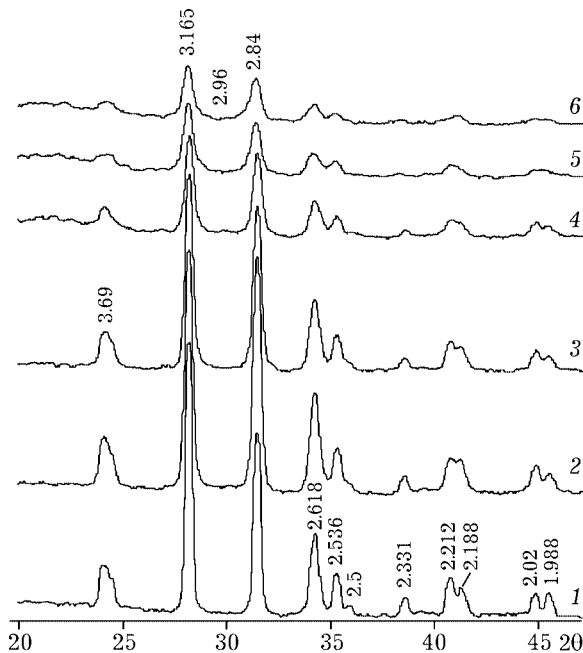Fig. 2. Crystallinity degree of M form of zirconium oxide depending on the time of treatment in a vibratory mill.

Fig. 1. Diffraction patterns of the products formed during the treatment of dry zirconium oxide powder of the monoclinic modification in a vibratory mill depending on mechanical loading: 1 – initial oxide, 2–6 – after mechanical treatment for 3 h (2), 4 (3), 9 (4), 12 (5), 15 h (6).
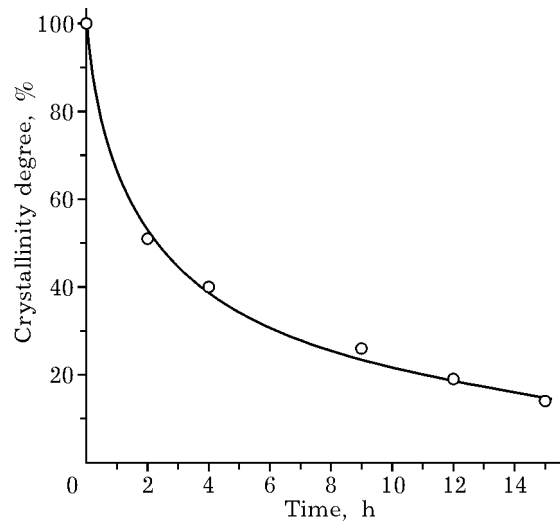
along with a decrease in the intensity and broadening of the reflections of the initial crystalline phase. After 15 min, the initial form of the oxide is almost absent while the obtained crystalline product is represented by the tetragonal ZrO_2. The presence of the cubic modification is also possible. Reliable identification is hindered because of the similarity of the diffraction patterns of this modification and the tetragonal form and because of substantial broadening of the lines. In the presence of water as additive, the phase transition started after 2 min; after 15 min, only a small part of the initial oxide underwent phase transition.

It is known that two main factors affect broadening of the diffraction reflections: a decrease in the crystallite size and the level of defect concentration in them. Different characters of the dependence of dimensional and deformation broadening on the reflection order allow distinguishing between these factors. According to [18], broadening of the β lines in the diffraction patterns is connected with the crystallite size D_G and with the mean square microdeformation $(e_G^2)^{1/2}$ by the following equation:

$$(\beta \cos \theta / \lambda)^2 = (1/D_G)^2 + 16 \, e_G^2 \, (\sin \theta / \lambda)^2$$

where θ is diffraction angle, λ is wavelength of X-ray radiation ($CuK_{\alpha 1} = 1.5406$ Å). With the help of this equation, one may separate the contributions by plotting the square
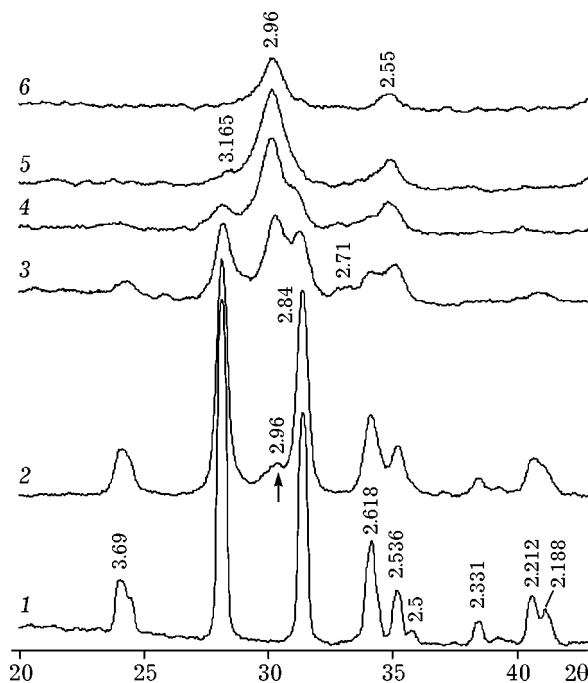
Fig. 3. Diffraction patterns observed after treatment of the dry zirconium oxide powder of monoclinic modification in a centrifugal planetary mill depending on mechanical loading: *1* − initial oxide; *2–6* − after mechanical treatment for 0.5 min (*2*), 2 (*3*), 5 (*4*), 15 (*5*), 22 min (*6*); arrow indicates the basic reflection for the tetragonal oxide.

dependence in the coordinates $(\beta \cos \theta / \lambda)^2$ − $(\sin \theta / \lambda)^2$. The slope angle of the straight line on the plot characterizes the mean square microdeformation, while the segment cut off the ordinate axis characterizes the size of crystallites. When determining integral broadening of lines, corrections were made for instrumental broadening of the corresponding line for well-crystallized ZrO_2.

The results of analysis of line broadening in the diffraction patterns of treatment products obtained in the vibratory mill are shown graphically in Fig. 4. Rather good convergence of the results for different crystallographic planes is observed, which is the evidence of isometric process. One can see that broadening of the lines occurs both due to the small size of crystallites formed during crushing and due to the defects in them. During the initial period of treatment (within the first 4 h), the slope angle of the straight lines is small. Crystallite crushing process prevails at this stage, resulting in some decrease in the level of microdeformations in small crystallites. After

4 h, their size is 38 nm, with the mean square microdeformation 2.1 10^{-3} (Fig. 5). An increase in the time of mechanical loading up to 15 h causes gradual accumulation of micro-deformations up to 5.4 10^{-3}. The size of crystallites remains almost the same (40−41 nm) and exceeds the critical size, which is 30 nm [7, 8] for the phase transition. In light of the obtained data, it should be noted that the anomalously small critical crystallite size (10 nm) reported in [10] for which the phase transition from the M form of ZrO_2 into T-form is observed cannot be considered as correct because it was calculated using Debye − Scherer equation without taking into account the effect of microdeformations on peak broadening. In the case under our consideration, a similar calculation of the size of crystallites obtained in the vibratory mill after 15 h would give 23 nm, which is approximately 2 times smaller.

A different picture was observed in the centrifugal mill. As early as after milling for 30 s, the mean crystallite size of the initial ZrO_2 decreased to 20 nm with the low level of microdeformations − 1.2 10^{-3} (Fig. 6). Further treatment caused gradual broadening of the reflections of both forms, which is likely to be connected with also with the accumulation of microdeformations. This oxide rapidly
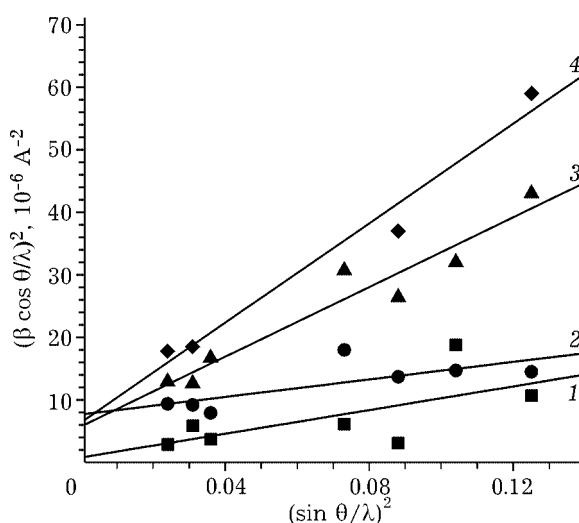

Fig. 4. Linearization of the experimental data on broadening of lines in the diffraction patterns of the products of mechanical treatment of M-ZrO_2 in a vibratory mill for 2 h (*1*), 4 (*2*), 9 (*3*) and 15 h (*4*) according to Williamson − Hall equation.
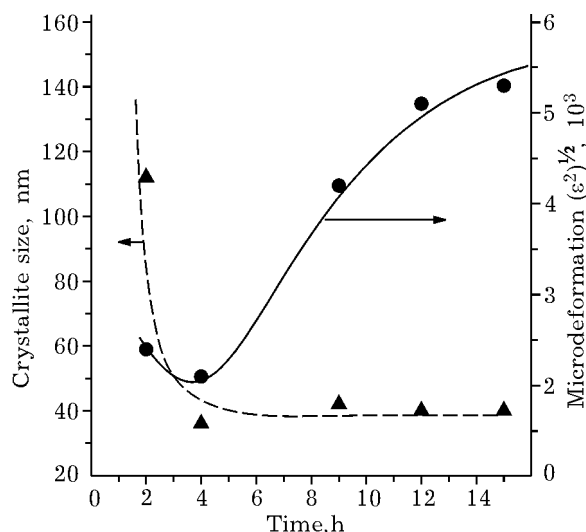
Fig. 5. Effect of duration of treatment of M form of zirconium oxide in a vibratory mill on crystallite size and level of microdeformations.

recrystallized into the tetragonal modification. Due to substantial broadening of the reflections of both phases, the neighbouring reflections overlapped, which hindered a detailed analysis of the diffraction patterns at the main stage of the phase transition. For activation in the presence of water, the initial stage (30 s) was characterized mainly by crushing with the formation of small crystallites (36 nm) with low level of microdeformations. With an increase in the time of action of the mechanical load to 2 min, microdeformations were accumulated in the crystallites (up to до $3.3 \ 10^{-3}$) almost without any changes in size and the nanostructured T form started to form.

So, the data obtained indicate that mechanochemical activation of zirconium oxide of the stable monoclinic modification in high-energy strain device stimulates crushing processes in crystallites and accumulation of microdeformations in them, which is accompanied by a rapid phase transformation into the tetragonal form. For comparison, it should be noted that the phase transition of M form into T form proceeded in the ball mill by 45 % only after 50 h [10]. It is likely that there are no reasons to assume that the phase transition follows exclusively the mechanism of thermal activation occurring at separate sites of a solid as a result of heating above 1172–1200 °C. Achievement of such a high

temperature is not probable in the centrifugal planetary mill [19] and is likely to be almost impossible in the ball mill.

Rapid reaction of phase transition in the mechanochemical apparatus is likely to proceed according to a complicated mechanism under the influence of a large number of factors. Some authors [1, 5] think that the existence of tetragonal zirconium oxide at low temperature is connected with its fine dispersed state. When T form is obtained by thermal activation, such a state is formed from the fine dispersed hydroxide precursor. The latter is doped with polyvalent cations (with the valence below 4), which hinder the growth of crystallites, as the authors of [1, 5, 6] assume. In the mechanochemical apparatus, intensive crushing of the crystallites as a result of high-energy mechanical action can cause the synthesis of the tetragonal form from the well-crystallized monoclinic form. Mean crystallite size decreases to 20 nm and below as a result of crushing, that is, the size region characteristic of the tetragonal form is achieved. In a vibratory mill, the power of mechanical impulses is insufficient for efficient crushing of the crystallites; according to [20], the strength of the latter increase with a decrease in size.
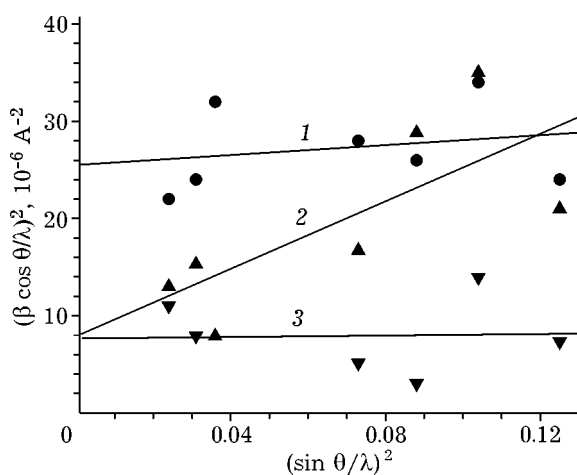

Fig. 6. Linearization of the experimental data on broadening of lines in the diffraction patterns of the products of mechanical treatment of M-ZrO$_2$ in a centrifugal planetary mill according to Williamson – Hall equation: 1 – treatment of the dry powder for 30 s; 2, 3 – treatment of the aqueous suspension for 30 s (3) and 2 min (2).

The phase transition during mechanochemical activation is likely to be connected with pulsed and extremal in intensity mechanical action, which lead to local increase in pressure and temperature in separate regions of a solid, as described in [20] for the first time. The transition of M form into T form is accompanied by a decrease in molar volume by about 7 %. It may be expected that the local increase in temperature and pressure under the action of mechanical impulse can provide thermodynamic probability of the formation of more dense T form in these regions. With an increase in mechanical loading, the structural changes can spread over the substantial part of the volume of a solid and further over its whole volume.

According to thermodynamic data [21], a linear correlation between the applied external static pressure and temperature point of phase transition is fulfilled for the zirconium oxide system: $dT/dP = -0.032$ deg/bar. It follows from this relation that at a pressure of 2 GPa, which according to [19, 22] can be achieved in local sites of a solid in a mechanochemical apparatus, the point of M $\rightarrow$ T phase transition should decrease by 640 °C, that is, to a level of 560 °C. The possibility of achieving such a level of temperature during mechanical activation was established in a number of works [19, 22]. The experimental data [23] on the effect of the applied external static pressure on phase equilibria indicate that the transition of monoclinic ZrO_2 into the dense rhombic modification (which is also metastable under normal conditions with respect to the monoclinic modification) occurs at a pressure of 2.0−2.5 GPa and a temperature of 450 °C. With an increase in pressure to 3.0−3.5 GPa, temperature decreased to 400 °C. According to the data of [24], the transition of M form into T form at 3.7 GPa was observed at room temperature.

It should be stressed that the relations considered above were established for phase transitions under the action of static pressure. A specific feature of the dynamic transitions under the shock action of powerful pressure pulses is that they occur under a sharp pressure gradient in the front of the shock wave, which generates a substantial number of defects and dislocations. As noted in [25], under these conditions a noticeable acceleration of the process and a decrease in the pressure of phase transition in comparison with the process caused by static pressure are observed.

It should be noted that substantial amount of iron is brought into zirconium oxide, which possesses rather large hardness, during treatment as a result of wear of the grinding balls and the cylinder. For instance, after treatment for 2 min, 3.5 % mass of iron is detected in the product. After 5 min, iron concentration increases to 8.0 %. Mass concentrations of such metals as Cr, Ni, Mn, Mo, Ti, V was less than 0.03−0.05 %. Iron introduced as a result of wear is mainly in the metal state, while the fraction of oxidized iron which can cause stabilizing effect on the formation of tetragonal form is insignificant. On the other hand, the data previously obtained by us indicate that the promoting action of the introduced Fe^{2+} ion additives on the mechanochemical process starts when their mass concentration in solution in not less than 2.3 %; for lower amount of this additive, it had almost no effect on the formation of the tetragonal oxide. It follows from this fact that the formation and stabilization of T form during mechanical activation is likely not to be connected to a decisive extent with the extrinsic iron arriving from wear, though it may affect the rate of the process. This is confirmed by the data of reported [10], where the phase transition of monoclinic zirconium oxide into tetragonal one was observed in grinding devices made of different materials: tungsten carbide, corundum, and steel.

CONCLUSIONS

The data obtained indicate that mechanochemical activation of zirconium oxide of the stable monoclinic modification in high-energy strain grinding apparatus stimulates crystallite crushing processes, accumulation of microdeformations, accompanied by a rapid phase transition into the metastable tetragonal form. The rates of the processes depend on the medium of treatment; the presence of water additives slows down the phase transition process. The treatment in a vibratory mill causes

mainly crushing of the crystallites, accumulation of microdeformations in them and amorphization of structure.

The formation of metastable tetragonal form of ZrO_2 in high energy strain mechanochemical activator can be due to the pulsed character of powerful mechanical action, which causes intensive crushing of the crystallites (J20 nm) and can create local conditions in separate sites of a solid, which would be favourable for the phase transition from the thermodynamic and kinetic points of view.

ACKNOWLEDGEMENTS

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