

Nature of a Mechanically Stimulated Phase Change in Zirconia

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Abstract

Reasons for phase change in zirconia upon its intensive mechanical treatment in mills have been discussed. It has been demonstrated that when used steel balls and barrels, oxidation of wear products and their mechanochemical interaction with ZrO_2 occurs along with a decrease in the size of particles and crystallites. It has been found that implantation of cations of an extrinsic metal in the crystal lattice is favourable to the stabilization of a more symmetric modification and to an increase in the critical size of crystallites, above which the monoclinic modification becomes stable. A conclusion has been made that an increase in the contribution of superficial energy to the Gibbs energy plays dominating part in the phase change on initial stages of mechanical treatment, while the thermodynamic stability in the further process is controlled preferentially by a stabilising impact of impurity cations. Under conditions that prevent from pollution of ZrO_2 by metal, a dynamic equilibrium is established between the forward change to tetragonal modification and the reverse, to monoclinic.

INTRODUCTION

It is common knowledge that phase changes into modifications that are thermodynamically stable only at high pressure and temperatures are often noted during the course of intensive mechanical treatment of solid bodies in mills-activators of various types [1–5]. It is generally agreed that this is an evidence for high impulses of pressure and temperature that are generated upon the impact of a milling body at the work material and upon quenching of a state that is non-equilibrium under ordinary conditions.

Change of monoclinic into tetragonal modification of zirconia has been discovered in 1976 by the authors of work [6] and it was observed later by many researchers in various experimental conditions (see, for example, [7–11]). In so doing, while the authors [11] suggest a non-equilibrium nature of the processes that occur in the mill as a principal cause of the observed phase change (which is traditional for mechanochemists), the authors of [6, 7] consider an increase in the specific surface of the grinded

powder and hence in the contribution of superficial energy to the Gibbs energy to be the crucial factor. Such assumption is based on a hypothesis [12], the essence of which lies in the fact that a superficial energy for the tetragonal modification of ZrO_2 is less than for the monoclinic one, and the monoclinic modification becomes unstable when the size of the crystallites decreases to reach a certain critical level.

Thus far, many works are published, wherein various methods are used to yield superfine powders of zirconia in tetragonal and/or cubic modification, but the discussion does not die out, whether the formation of highly symmetric phases is determined by kinetic reasons or they really are thermodynamically stable due to their size [13]. However, in our opinion, the authors of the work [14], wherein it has been demonstrated that the annealing of a nanocrystal mixture of tetragonal and monoclinic phases under conditions that hinder the growth of the particles yields the complete change exactly to tetragonal modification, give a convincing evidence for the stability of the highly symmetric modification in the nanocrystal state. It

has been proved experimentally in [15] somewhat later that the allowance for the parameters that are related to superficial energy and the bubble pressure in the expression for the Gibbs energy yields a dependence of the temperature when monoclinic modification changes into tetragonal one on the reciprocal size of the particles. This resulted in that it has been possible to define the critical size of particles, below which the tetragonal modification is stable at ambient temperature. This magnitude was equal to 22.6 nm, which is extremely close to the values that were determined by various experimental techniques [16–18]. The authors of [19] succeeded in experimental determination of an excess enthalpy of nanocrystal tetragonal, monoclinic, and amorphous ZrO_2 and succeeded in demonstrating that as the surface increases by a mole of the oxide, the tetragonal first and then the amorphous phase must become thermodynamically stable. Thereafter, an assumption can be deemed to be proved that a lower superficial energy of highly symmetric ZrO_2 phases determines their thermodynamic stability in the nanocrystal state.

Hence, the hypothesis that the mechanically stimulated phase change that is observable in ZrO_2 in various types of mills is caused by the non-equilibrium nature of the processes possibly appears to be bankrupt. Meanwhile, it is pointed out in [10, 20] that the interpretation of experimental results that were received upon intensive grinding of ZrO_2 involves difficulties if a decrease of the particle size is believed to be a principal cause of the observed phase change. The authors take note of the fact that according to models suggested in [20], the intensive mechanical grinding must lead to a state of dynamic equilibrium (when the rates of grinding and recrystallization are identical) and to equilibrium size of the particles of the grinded material. This is responsible for a situation that was observed in [6, 8] when the degree of a phase change reached approximately 40 % and it was further unaffected in time. On the other hand, 100 % tetragonal modification has been obtained in [7, 9, 10] for a rather short time. It should be noted that the works [6, 8] used milling bodies and barrels from tungsten carbide, and the works [7, 9, 10], from steel. An assumption has been proposed about the

involvement of iron impurity in the observed phase change that has been formed owing to a wear of milling bodies. It was admitted separating of ZrO_2 particles by metal that would retard recrystallization, as in [21], or introducing iron cations into the crystal lattice of the oxide and the subsequent stabilization of highly symmetric modifications.

Once mechanochemical reactions $ZrO_2 + Fe_2O_3$ have been performed in works [8, 22] with the formation of a tetragonal solid solution that contained as much as 20 mol. % of iron oxide, and once it has been demonstrated in [23] that even 0.7 % of iron that had been introduced into amorphous oxyhydroxide zirconium led to preferential formation of tetragonal modification upon the subsequent heat treatment and 2 mass % of the metal would suffice for its full stabilization, the point of view that has been suggested in [21] became still more urgent.

This work is devoted to a more detailed study of a mechanically stimulated phase change in ZrO_2 and part played by impurities in that process.

EXPERIMENTAL

A ZrO_2 powder of qualification “kh. ch.” (chemically pure) was used in the work. The X-ray diffraction analysis identifies a well-crystallized monoclinic modification without impurity of other phases with the size of crystallites on the verge of the detection limit of the method described below, *i.e.* approximately 0.2–0.3 nm.

X-ray investigations were performed in a DRON-4 diffractometer, $CuK_{\alpha 1}$ radiation with a graphite monochromator at a rate of 0.25–0.5 deg/min. A relative content of phases and the size of crystallites were determined by the Rietveld method using the Powdercell code. To describe a profile of lines the use was made of the PsVoigt1 function and lattice constants of zirconium oxide modifications were varied additionally. The analysis of expressly prepared mixtures of zirconium and aluminium oxides has demonstrated that the accuracy of determination of the composition was at a level of 5 rel. %. Sizing of crystallites was conducted with all reflexes in the angle range of 20–80° (2 θ) and with the line width of the reference

substance that has been determined in the same conditions of obtaining the spectra (0.15–0.20°).

Mechanical treatment was conducted in AGO-2M planetary mill with accelerations that reached 15 to 40g. Steel balls (ShKh-15) and wear-resistant balls from ZrO₂ of the TOSOH Corp. (Japan) were used. Balls and inserts in steel barrels that have been constructed of α -Al₂O₃ were applied in particular experiments. Water or a mixture of water and ethylene glycol that were forced by a pump with a constant flow rate was used as a liquid that cooled the barrels. A temperature of the refrigerating liquid was varied in the range 0–120 °C by means of a thermostat with adding ice (if necessary).

The iron content of samples was controlled by the flame photometric method. Solutions that were received upon treatment of powders by etching acid and nitrohydrochloric acid were analysed. In the former case, the substance dissolved completely, and in the second, it was assumed that only iron that formed because of the wear of the milling instrumentation dissolved, since pure ZrO₂ is stable against nitrohydrochloric acid. The difference of the results of the analysis, in our opinion, matched the quantity of iron that has embedded into the crystal lattice of ZrO₂.

Annealing of samples was conducted in a muffle for 1 h with an accuracy of the temperature control of 5 °C in the air or in a foil from aluminium or stainless steel at the temperatures of 500–1100 °C depending on the chosen material. A bag from the foil was put on the bottom of a covered porcelain crucible under a thick layer of acetylene black to prevent access of oxygen.

RESULTS AND DISCUSSION

From Fig. 1, one can see that roentgenograms of the samples that have been obtained upon ZrO₂ grinding with a low and high temperature of the refrigerating fluid differ essentially.

Figure 2 presents the dependence of the degree of phase change (DPC), *i.e.* the ratio of the quantity of tetragonal modification that has formed upon grinding to the total quantity of ZrO₂, on temperature. Let us note that roentgenograms of the samples that have passed

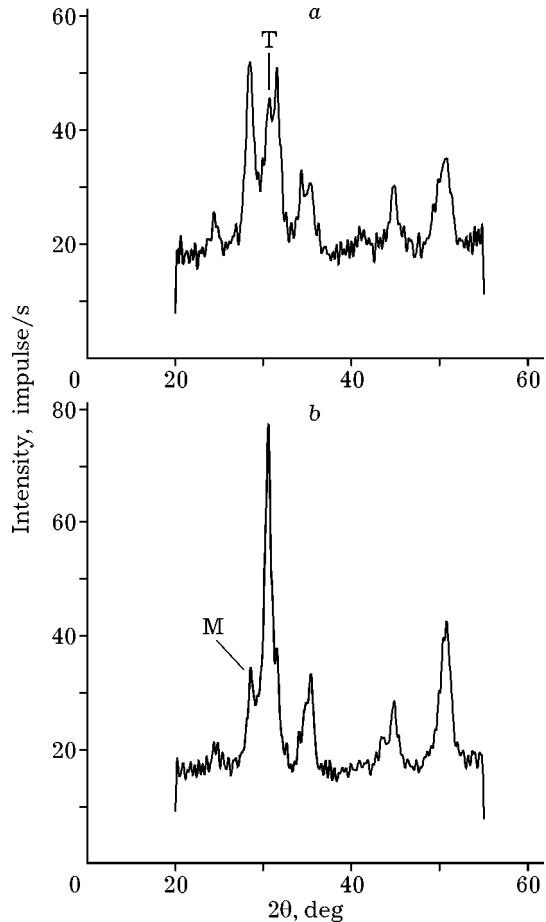


Fig. 1. Diffractograms of zirconia samples that were grinded at the temperatures of 5 (a) and 88 °C (b). Grinding time was 21 min, 10-mm steel balls, acceleration of 20g; T – tetragonal, M – monoclinic modifications.

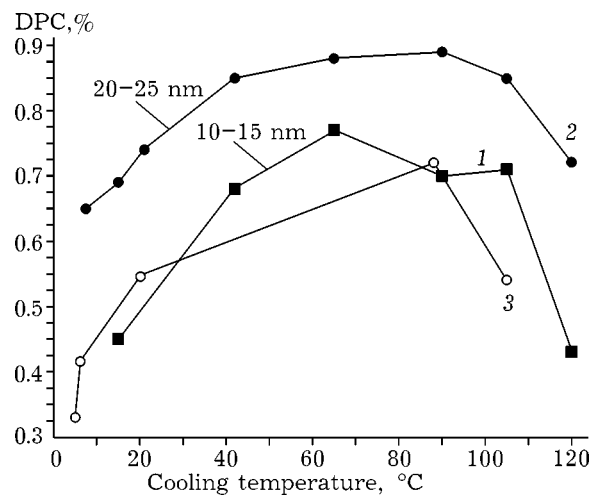


Fig. 2. Change of the degree of phase change (DPC) of monoclinic ZrO₂ modification to tetragonal upon grinding by steel balls depending on temperature of the refrigerating liquid. Processing conditions: 1 – 40g, 5-mm balls, 15 min; 2 – 40g, 10-mm balls, 15 min; 3 – 20g, 10-mm balls, 21 min. Numbers near curves are the size of the crystallites.

mechanical treatment are strongly broadened and do not permit unambiguous interpretation of the formed modification as tetragonal or cubic. Henceforth, this modification will be considered to be tetragonal, since the roentgenogram unambiguously identifies it upon the annealing at 900 °C (see Fig. 4, c below).

It has been found that the DPC achievable for a certain time grows with an increase in temperatures of the refrigerating liquid, passes through a maximum and then drops significantly. The size of crystallites of the formed tetragonal phase comprises 20–25 nm upon grinding by balls of diameter 10 mm and 10–15 nm when used 5-mm balls and it is independent of the DPC. Moreover, the powder that is grinded by balls of smaller diameter and that is composed of finer crystallites is characterized by substantially smaller content of tetragonal modification at all temperatures of refrigerating liquid.

The experiments that have been lead with the use of a barrel and balls from α -Al₂O₃ have demonstrated that, although the size of crystallites of the monoclinic phase drops to reach 15–16 nm, DPC comprises just 23 %, and it is substantially lower than the values obtained with steel balls even in the case of larger size of the crystallites.

Upon heating of certain grinded samples with no access of oxygen (Fig. 3, Table 1), the size of crystallites increases up to 70 nm, which considerably exceeds all theoretical and experimental estimates of the critical size. In this case, an inverse transformation into monoclinic modification must occur; however, no transformation is observed. The inverse transformation into monoclinic modification is realized at 800 °C in the oxygen-free medium and at 950 °C in the air and it does not show obvious correlation on the size of the crystallites. Consequently, the stability of tetragonal

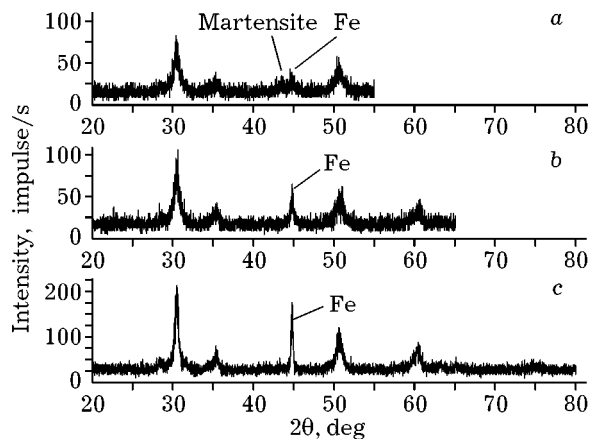


Fig. 3. Diffractograms of ZrO₂ samples that were grinded by steel balls (10 mm, 40g, 15 min) and annealed at 25 (a), 500 (b) and 700 °C (c) in the oxygen-free medium. Temperature of the refrigerating liquid was 105 °C.

modification in these conditions must be controlled by alternate reasons rather than the size of the crystallites.

Discussion of the nature of the dependence of DPC on the temperature of refrigerating liquid is beyond the scope of the research; however, the following is evident. The above results are not consistent with a hypothesis that a mechanically stimulated change is caused by a decrease of the particle size and once an increase in the contribution of superficial energy to the Gibbs energy is of importance, it is not a single factor that determines the DPC magnitude.

Table 2 lists the results of chemical analysis for the content of iron oxide of certain samples that have been obtained under various experimental conditions.

With allowance made for the fact that ZrO₂ becomes soluble in nitrohydrochloric acid (up to 10–15 %) after the mechanical activation, the iron content that is given in Table 2 may even appear to be somewhat underestimated. From these data it follows that a significant amount of iron cations is embedded into the

TABLE 1

Dependence of the sizes of crystallites and DPC of grinded ZrO₂ on the annealing temperature

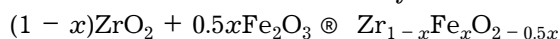
Temperature, °C	Size of the crystallites, nm	DPC, %	Parameters of the cell, Å
25	19	85	5.104
500	39	83	5.098
700	71	84	5.101
850	–	2.5	–

TABLE 2

Content of iron oxide in the crystal lattice of grinded ZrO_2 as a function of the conditions of the mechanical treatment

Acceleration	Diameter of the balls, mm	Temperature of the cooling liquid, °C	Grinding time, min	Quantity of Fe_2O_3 , mol. %
40g	10	25	25	4.5
40g	10	42	15	6.0
40g	10	>105	15	4.1
40g	5	90	15	2.2
40g	5	>105	15	1.0
20g	10	88	21	3.1

ZrO_2 lattice and possibly stabilises tetragonal modification. According to [23], the quantity of cations would suffice to provide the observed DPC values. Let us note that the content of iron that has entered into zirconia is the higher, the more the energy of the grinding ball that decreases within the succession: 40g – 10 mm, 20g – 10 mm, 40g – 5 mm. This is to be expected, for the speed of the conjectured reaction of mechanochemical synthesis



is controlled by the intensity of plastic strains and by the volume, wherein they proceed upon a unit action of a ball on the mixture of reagents.

To compare the data we received with the results of the work [8] where it has been assumed that a solid solution that has formed by mechanochemical interaction of ZrO_2 and iron and that contained 5 mol. % Fe_2O_3 shows cubic modification with the parameter of the cell that was equal to 5.093 Å, the values that were presented in Table 1 have been also calculated for the cubic lattice. The lattice parameter remains constant upon thermal annealing (within the limits of 0.1 rel. %) and with computation according to the formula that has been suggested in [24] matches the cubic modification of ZrO_2 that incorporates 3 mol. % Fe_2O_3 that is comparable to the data of Table 2. This is testimony in favour of chemical reaction that passes as a result of the mechanical treatment and the formation of ZrO_2 stabilised by iron cations.

The diffractogram that is presented in Fig. 3, a contains in addition to reflexes of tetragonal ZrO_2 modification, reflexes of carbonaceous iron (martensite) and α -Fe at the re-

spective 2θ that are equal to 43.4 and 44.7°. Upon the annealing in this range of angles, the narrow and intensive reflex appears, from which it is possible to recognize the presence of α -Fe in the samples with the content at a level of 1 mass %. This circumstance becomes extremely important during the analysis of data of Fig. 4 that displays the transformation of the roentgenogram of the sample that has been mechanically processed with steel balls until practically complete transformation into the tetragonal modification is reached, after washing of iron in muriatic acid and the subsequent air annealing at the temperatures of 900 and 1000 °C. While the roentgenogram at 900 °C shows the 100 % tetragonal modification of ZrO_2 without impurities of any other phases, a phase change into monoclinic modification and simultaneous emergence of α - Fe_2O_3 (hematite) peaks is evidenced at 1000 °C. These data agree well with the electron diffraction studies that have been performed in [22] for a mechanochemically synthesized solution that contained 18 mol. % of Fe_2O_3 .

The quantity of hematite we determined by the Rietveld method was equal to 4.8 mol. % and it accords well with the magnitude that has been received upon chemical analysis (see Table 2) of metal oxide that has entered the crystal lattice (4.5 %). The formation of hematite may be related only with the availability of iron cations that are dissolved in tetragonal modification of zirconia, since the sample that has been annealed in the oxygen-free medium at 700 °C and previously washed in HCl (not shown in Fig. 4) does not contain reflexes of α -Fe and, as was highlighted previously, it may contain no more than 1 % of the substance.

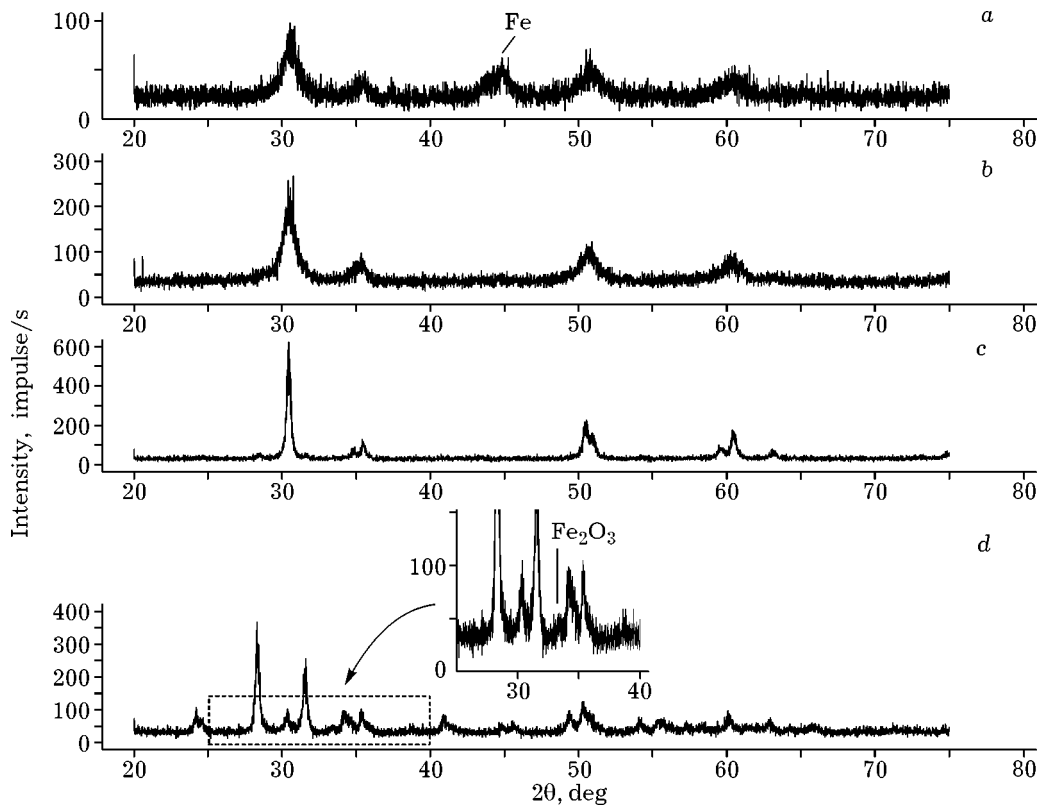


Fig. 4. Diffractograms of ZrO_2 sample that was grinded by steel balls (10 mm, 40g, 25 min) (a), next washed with HCl (b) and annealed in the air at 900 (c) and 1000 °C (d).

Thus, one can argue that iron cations not simply enter the ZrO_2 lattice, but stabilise its highly symmetric modification in much the same manner as cations of yttrium, calcium, *etc.* Upon a sufficient mobility of atoms is attained, a solid solution that is metastable under these conditions breaks up, with the result that the stabilising effect of iron cations disappears and the conversion into monoclinic modification occurs. The analogous explanation of thermal decomposition of mechanochemically synthesized $Ca_{0.2}Zr_{0.8}O_{1.8}$ and $Mg_{0.2}Zr_{0.8}O_{1.8}$ is given in [25]. The bare fact that the solid solution that is stabilised by iron and is metastable at these temperatures is supported by much lower temperature of disintegration in the medium with a low fractional pressure of oxygen, although it is common knowledge that thermodynamic stability of tetragonal ZrO_2 and solid solutions around it under conditions of deficit of oxygen, on the contrary, shows a rise [26–28]. The disintegration begins upon reaching a sufficient diffusive mobility of elements of the crystal lattice, and it, certainly, rises with an increase

in the number of anionic vacancies that is ensured by the low pressure of oxygen.

The set of the given results testifies that upon the high-intensity grinding of zirconia in a steel medium, the oxidation of the grinded metal occurs and the subsequent mechanochemical synthesis of $Zr_{1-x}Fe_xO_{2-0.5x}$ metastable solid solution. Indeed, upon the mechanical treatment is performed over the course of 20 min with 20g in argon atmosphere, the DPC appreciably decreases as compared to that upon the air treatment (38 and 58 %, respectively). An assumption can be made that the impossibility to oxidize the grinded metal by air oxygen hinders carrying out the mechanochemical synthesis.

Meanwhile, the limiting quantity of Fe_2O_3 that can be formed and subsequently can be included into the lattice of ZrO_2 upon complete running out of oxygen that is in a tight barrel in the form of water molecules that are adsorbed on the powder and that are present in the gas phase and air oxygen is as great as 2 mol. %. However, according to chemical analysis, the quantity of Fe_2O_3 that is embedded

into the lattice, on occasion, exceeds it 2–3 times. It appears that an additional source of oxygen is the ZrO_2 itself that exhibits a large nonstoichiometry and thus it can give oxygen atoms for the formation of Fe_2O_3 .

Hence it follows that attempts to avoid the contamination of the crystal lattice of the grinded ZrO_2 by removing the moisture and air from a barrel of the activator and to prevent thereby the oxidation of iron are doomed to failure. The use of steel milling bodies and barrels is always attended with a danger that iron impurities embed into the lattice that cannot be removed later.

We made an attempt to prevent the interaction of the grinded iron with zirconia. For this purpose acetylene black was admixed to the dioxide (10 mass %), and the mincing barrel rotated on spherical mill for 30 min prior to the treatment in a planetary mill. It was assumed that either carbon black becomes the preferential absorbant of oxygen, or it will link the grinded iron to form carbides, or it will simply separate iron and dioxide from each other. Appreciable decrease of DPC was expected in all cases, which was exactly what occurred in the experiments. The most clearly defined results have been received when used steel barrels and balls from tungsten carbide

(Fig. 5), because the quantity of grinded iron sharply drops in this case.

Scarcely any phase change can be observed even for 20 min of treatment, while the DPC reaches 25 % without carbon black even for 10 min. In so doing, the size of crystallites of the monoclinic phase is approximately 2 times greater; this may be related to the absence of the effect of the particle sorting mechanism. However, in our opinion, to understand the sequence of stages of the mechanochemical synthesis, the most remarkable feature is the circumstance that the process of transformation does not stop on addition of carbon black on the second 10 min of grinding. This is demonstration that the reaction of mechanochemical synthesis passes through a stage of the formation of aggregates from the reagents, and the interaction of the components at the subsequent stages occurs inside the aggregates. Adding carbon black during the second 10 min can no longer prevent the interaction inside the aggregate that has arisen earlier.

Let us note that although, in our opinion, we have reliably established the fact of the stabilising influence of iron cations that were implanted in ZrO_2 , we failed to obtain a strict correlation between the quantity of iron that is in ZrO_2 according to chemical analysis and the DPC magnitude.

By this is meant that the degree of phase change is controlled by a cumulative effect of a dimensional and chemical factor. On the one hand, the proportion of particles with the size that is less than the critical one gradually rises during intensive mechanical treatment in a mill. On the other hand, as the mechanochemical synthesis proceeds, the critical size of particles increases as it was shown in [15] for a case with yttrium cations that are implanted in the lattice of zirconium oxide. Both of the factors make for the transformation in the tetragonal modification and act simultaneously, but apparently to a different extent and at different stages of treatment.

In our opinion, this can be descriptively shown in studies of kinetics of a mechanically stimulated phase change using the balls from ZrO_2 and the subsequent annealing of samples (Fig. 6). In this case, the quantity of the grind-

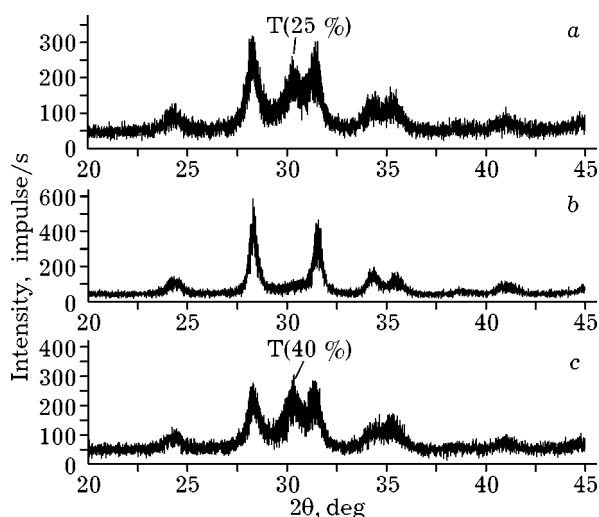


Fig. 5. Diffractograms of ZrO_2 samples that has been grinded by balls from tungsten carbide (20g, 10 mm) over the course of 10 min without adding carbon black (a), 20 min with carbon black added (b), and with carbon black added during the second 10 min of the grinding (c). The arrows show the reflexes that correspond to tetragonal modification; its content is in parentheses.

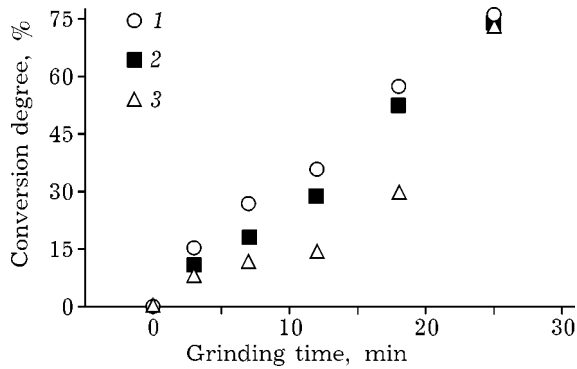


Fig. 6. Dependence of the conversion degree of ZrO_2 monoclinic modification into tetragonal modification during mechanical treatment with balls from ZrO_2 (25g, 10 mm) on the treatment time (1), with the subsequent annealing at 800 (2) and 900 °C (3).

ed iron sharply drops and reaches less than 2 mass % during the course of 20–25 minutes, which allows one to believe its effect to be insignificant at small times of treatment. It has been apparent in the kinetic curve that there is an inflection approximately at 12.5 min of the treatment and the inflection becomes more and more distinct after annealing the powders. The sizes of crystallites that make up the powders grow upon heating, and they vary, for example, from 16 to 40 and from 18 to 36 nm for the samples that were processed over the course of 12.5 and 25 min, respectively.

Growth of particles for the samples that were obtained at small times of mechanical treatment is accompanied by the reverse transformation of tetragonal into monoclinic modification since the transformation in this case is caused by a dimensional effect. With an increase in the treatment time, the reaction of mechanochemical synthesis with the grinded iron has the increasing effect, thus making for the increase of the critical size of particles. Therefore the influence of thermal annealing on the stability of tetragonal modification weakens gradually and, at last, 25 min of the treatment is sufficient to preserve cubic modification throughout the temperature range. About 2 mass % of iron is implanted into the lattice for this time, which is quite enough for the full stabilization of tetragonal modification. It is evident that annealing at the temperatures that cause disintegration of the solid solution (1000 °C) leads to the complete transformation into the initial phase state.

Thus the observed phase change is a result of two processes with various kinetics that occur in parallel. If the decrease of particle sizes begins right away, then the reaction of mechanochemical synthesis requires an induction period that is necessary to grind iron, to form aggregates from the grinded ZrO_2 and metal particles, and to oxidize metal. By virtue of a mechanochemical equilibrium that is attained according to the model [20], we succeeded to perform only partial transformation to form a more symmetric phase solely through grinding, with no application of special measures to prevent the recrystallization, in full agreement with data of [6, 8].

The bare fact that at least partial transformation is possible under conditions that eliminate completely the influence of any stabilizing cations is confirmed by data in Fig. 7. It is not ruled out that according to the results of experiments with the use of balls and barrels from tungsten carbide that are described in the literature, cobalt cations in much the same way as iron play the part of stabilizing ions. Cobalt to the extent of 6 or 8 % is applied as a binding agent in manufacture of products from tungsten carbide.

As it was mentioned above, the DPC magnitude that is achievable in treatment with balls from $\alpha-Al_2O_3$ in barrels with the same inserts does not exceed 20 % and this is the case just over an extremely narrow interval of grinding parameters. It is related, on the one hand, to a negative change in the kinematics

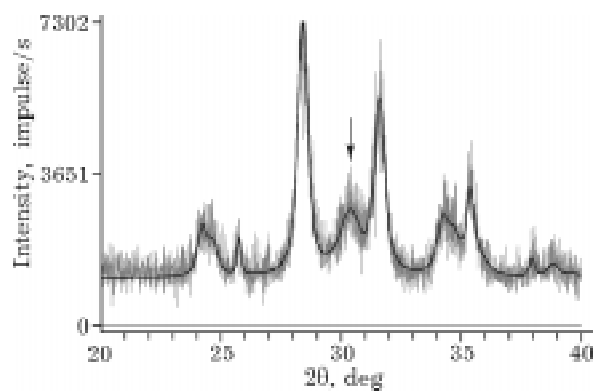


Fig. 7. Fragment of a diffractogram of ZrO_2 that has been grinded with the use of corundum balls and barrels and that was annealed at 800 °C. The arrow shows a reflex that identifies the tetragonal phase.

of ball movement upon a decrease of the inner diameter of the barrel and, on the other hand, to the impossibility to considerably increase the treatment time in view of the fragility of balls and bushings. Diffractograms of ZrO_2 powders that have been grinded with the use of corundum barrels and balls make impossible a reliable detection that tetragonal modification appears with its little content; however, the doubts that it is possible to perform the mechanically stimulated phase change under "clean" experimental conditions disappear after the samples are annealed at 800 °C (see Fig. 7).

CONCLUSION

Upon an intensive mechanical treatment of ZrO_2 in the steel medium, a phase change of monoclinic into tetragonal modification occurs, the degree of which is controlled by the treatment intensity and time.

The phase change is caused by two processes that proceed in parallel. At the initial state, the contribution is determined for the most part by a decrease of the particle size and by an increase of the contribution of superficial energy to the Gibbs energy of the phases. As the process develops, the stabilization of highly symmetric modification by iron cations that are implanted into the crystal lattice has the increasing influence. Upon ZrO_2 treatment in the medium that excludes the presence of metal, the degree of the transformation drops considerably and reaches the limit when the speeds of the processes of grinding and coalescence become equal and the system comes to the state of the dynamic equilibrium. The resulting tetragonal modification is thermally unstable and it transforms to monoclinic upon heating up to 700–900 °C. A temperature limit of the stability of the tetragonal phase is controlled by the fractional pressure of oxygen.

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