The Peculiarities of a-Al_2O_3 and ZrO_2 Nanogrinding

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Abstract

The scheme is presented describing the complex of principal physicochemical processes under intensive mechanical treatment of inorganic oxides as dynamic equilibrium between particle powdering and coalescence, and its graphic illustration is given. A large body of experimental results on superfine grinding of a-$A1_2O_3$ and ZrO_2 have been interpreted within the framework of the mentioned scheme. It has been shown the way this scheme is usable to optimize the method of solving particular problem of practical use: either produce fine and non-aggregated powder of $A1_2O_3$, or conduct the mechanochemical reaction of stabilized ZrO_2 synthesis for subsequent realizing of ceramic materials. Mechanisms responsible for contamination of treated powders by milling media stuff have been considered.

INTRODUCTION

The capacity to produce nanoceramic oxide powders determines greatly the speed of today's materials technology development. On the one hand, the decrease in particle size to less than 0.1 mm modifies and (or) enhances a number of consumer properties of powder materials; on the other, creating of uniquely featured materials with voluminous nanostructure [1–5] might be possible only through adoption of technology for generation of weakly agglomerated powders of the average size about 10–50 nm.

Mechanochemical grinding of oxides (and if submicron range particles are mechanically treated, concurrent physical and chemical processes proceed in ensemble and interrelationship) has certain advantages against other powder production methods. This technique is rather cheap, ecologically clean, for it is not bound up with use of large volume of liquids, and makes it possible to obtain desirable size particles. At the same time, simplified concepts of average particle size correlation with intensity and (or) grinding time, true for rough milling, that more time and intensity of material treatment give less average particle size, appeared to be completely inadequate for the submicron range.

Present concepts of superfine milling that takes place in ball, vibratory, planetary and other mills, can be qualitatively illustrated by Fig. 1. With the decrease in particle size, the correlation between gravitational and superficial forces changes in favour of the latter ones, which is that results in formation of fine particle aggregates (agglomerates). Subsequently, one can observe transformation of loose and frail aggregates into stable and considerably more compact formations, that has an effect on specific surface value, internal porosity of powders and size of separate formations in suspensions and aerosols. At that stage the decrease of particle size alternates to increase due to the fact that the particle then constitutes an aggregate.

The next stage is connected with changes to an aggregate that is, by that moment, a polycrystalline particle formed by particular crystallites. Crystallites merging and disappearance of the partition borders between them (recrystallization or particle coalescence) occurs. The process is made considerably easier by exterior pressure applied. The system then transfers to the state of dynamic equilibrium determined by particular conditions in mechanochemical device. The processes of crystallites (grains) reduction occur concurrently with the process-

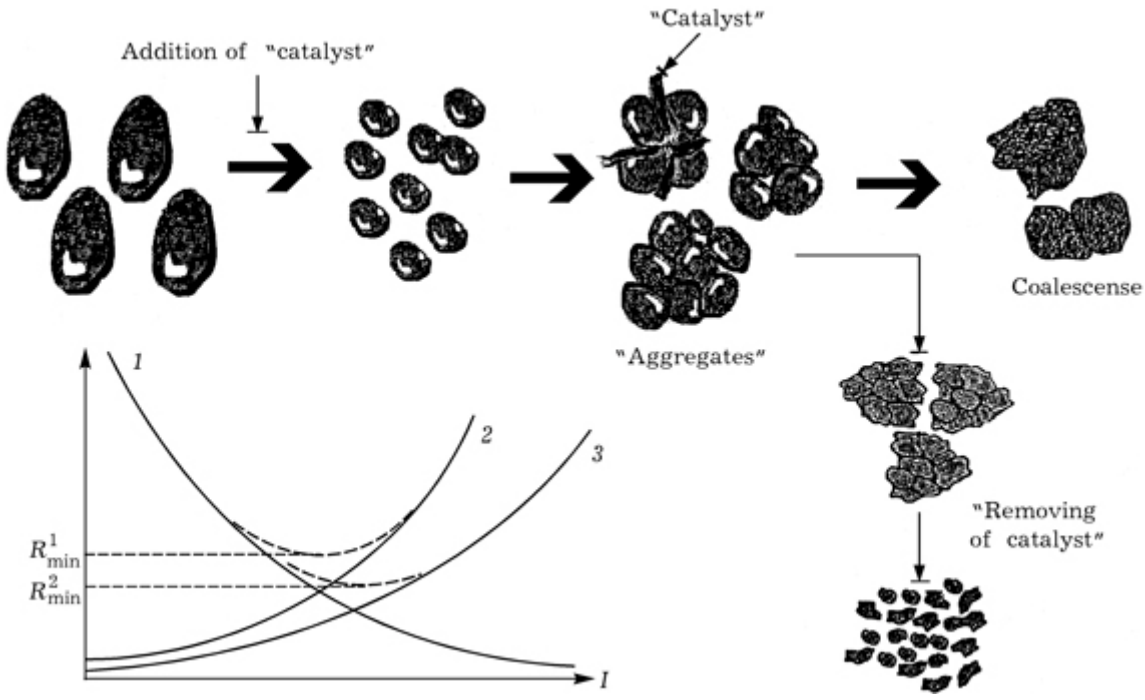

Fig. 1. Scheme of the nanogrinding process mechanism and its graphic illustration: *1* – grinding, *2* – aggregation, *3* – crystallite coalescence.

es of its growth, thus further decrease of average crystallites size becomes impossible.

Said above is illustrated by qualitative chart (see Fig. 1). Curve *1* depicts the decrease of particle size with the increase of time or mechanical action intensity, whereas curve *2* describes the aggregate formation process. The more is the intensity of action on the collection of particles, the bigger particles can be joined into aggregate. The curve depicts also the evident fact that the particles, which size is less than the critical one for the given conditions, are subject to spontaneous aggregation. The resulting parabola defines the minimum achievable particle size in these circumstances. Curve *3* describes the process of crystallites growth, and minimum achievable crystallite size is defined by parabola formed by curves *1* and *3*.

Correct interpretation of grinding results in accordance with the chart described allows one to optimize the way toward desirable results. It becomes clear that in some cases decrease of particle size is possible under decrease of grinding time or intensity, and the powder with the average size less than minimally determined by Fig. 1 is obtainable only under different treatment conditions. The object of the present work is to illustrate the employment of the scheme suggested in Fig. 1 by the concrete examples of mechanochemical treatment of alumina and zirconium oxide.

EXPERIMENTAL

Zirconium and aluminum oxides of "chemically pure" ("kh. ch.") and "analytically pure" ("ch. d. a.") type have been used in this work. Aluminum oxide was previously calcinated at 1150 °C to complete conversion into a-modification. Zirconium oxide would constitute initially a pure monoclinic modification.

Mechanical treatment was performed in the planetary mill AGO-2M. For experiments with the balls of varied effective density, the steel balls with bored holes have been used. Balls density was calculated as ball weight divided by circumscribed sphere volume. Specific surface of samples was measured by BET-method under thermal argon desorption. Crystallites size was determined by breadth of (012) and (024) aluminum oxide X-ray lines. Aluminum oxide calcinated at 1700 °C has been used as reference to account for other factor contributions in the line width. Contribution to line

TABLE 1

The effect of mechanical treatment time on Al_2O_3 grinding (20 *g*, balls and rollers of Al_2O_3)

Grinding time, min	Crystallite size, nm	Specific surface, m^2/g
0	195	6.4
5	100	
10	65	12
20	63	11

breadth associated with the change of crystallites size was filtered from contribution caused by microdistortions of crystal lattice according to [12]. X-ray study was performed on DRON-4 diffractometer, CuK_{a1} with graphite monochromator.

RESULTS AND DISCUSSION

a-Al_2O_3 grinding

a-Al_2O_3 mechanical treatment in the rollers with inserts and balls of the same material (20 *g* acceleration) is testimony to strong slowdown of grinding with time (Table 1). Powders therewith treated for 10 and 20 min are yet notably aggregated, since the particle size value of ~130 nm calculated from specific surface is substantially more than crystallite sizes given in Table 1. It seems logical to assume that experimental points lay around the *1–2* and *1–3* curves minima (see Fig. 1) and further increase of time of mechanical treatment would not result in decrease of particle and crystallites size.

Curve of *1–2* type, but in "specific surface – grinding time" coordinates, is observed under mechanical activation of many inorganic substances when using steel rollers and balls [13], and is linked traditionally to aggregation process development. Such curve for Al_2O_3 grinding is given by us in [14]. Symptomatically that the maximum values of specific surface obtained in [14], 14 m^2/g, are close to maximum values given in Table 1, though mechanical treatment conditions vary substantially. This is evidence for objective nature of *1–2* curve, dependent on aluminum oxide properties, but not on grinding device parameters.

It is apparent that similar curve can be plotted by varying both time and intensity of mechanical action. For example, Table 2 illustrates the influence of grinding media density. Dependence of specific surface on the ball density is of extremum character, forecasted by *1–2* curve, and it is specific surface that, by our opinion, accounts for the size of particles and compact aggregates. Though the hit power is growing proportionally to the increment of ball density, the specific surface of powder reaches some value and then goes down.

Fragility of tungsten carbide balls results in considerable contamination of powder, being ground, by abrasion products and thus leads to ambiguous interpretation of specific surface values.

For that reason, the specific surface was not measured. However, this circumstance does not preclude the crystallite size determination, and the presence of the curve of *1–3* type also comes evident.

Figure 1 presents an illustration of theoretically based in publication [15], and implemented in [16], change in grinding conditions through incorporation of inert substance, "grinding catalyst", into powder being ground , so that this

TABLE 2

The effect of ball density on Al_2O_3 grinding

Grinding time, min	Ball material	Effective density of balls, g/cm^3	Specific surface, m^2/g	Crystallite size, nm
20	Al_2O_3	3.9	12	63
15	Steel	3.9	11	51
15	»	5.4	17.5	
15	»	8	8	45
15	WC	16–17	–	66
15, 5 % Al	WC	16–17	–	39.5

substance separates the aggregate particles from each other and prevents them from merging back. In this case the curve *3* shifts into the area of large impact intensity (rightward), and the possibilities for further reduction of particle size arise. The position of the curve *1–2*, however, does not change significantly, and, moreover, it can move to the opposite direction, since "grinding catalyst" may promote the particle gluing to each other and the aggregate formation. It has been demonstrated with aluminum oxide in publication [16] the way the use of such "catalyst" makes possible an observation of the crystallite size reduction in the area, where the powder specific surface falls down, and the way the subsequent removing of the "catalyst" results in fine powder generation.

The same effect stems from the crystallite size variance in the case when ceramic and steel balls of similar density are used (see Table 2).

Incorporated into the powder, being treated, as the result of grinding media and rollers abrasion, the iron is capable of separating the particles to some extent and hamper the coalescence process. Because of this, the crystallites for the case of steel balls of ~4 g/cm^3 effective density, are somewhat smaller than for the case of ceramic balls. It should be noticed, that prolonged intensive grinding, bringing the particle size down up to dozens of nanometers, under conditions excluding coalescence, leads usually to monocrystalline powders. In this case the notions of crystallite and particle become synonyms.

It follows from the data presented in Table 2 that, with increase of ball density, the crystallite size at first decreases in a similar way, but then grows in accordance with the curve *1–3*. The fact, that it is the crystallites coalescence in the aggregates, which this growth is connected with, is confirmed by the experiment with the 5 % aluminum powder incorporated into the target powder to prevent the crystallite contact with each other. That is equivalent to curve *3* shift to the right, and in consequence the crystallite size has drastically dropped down.

Hence, it becomes evident that the production of the powder with the particle size less than some minimally achievable is available only through expressly changed conditions of grinding in order to move the curve *3* rightward and (or) the curve *1* leftward (see Fig. 1). The minimally achievable particle size for a-Al_2O_3 is about 50–60 nm. The increase of power intensity of the mill makes no more sense, that is confirmed by data [14] for centripetal acceleration reaching 40 *g*.

On the contrary, use of "grinding catalyst" under 20 *g* acceleration for 10 mm steel balls and treatment time of 15 min allows one, after subsequent removal of "catalyst", to obtain the powders of the specific surface equal 27 m^2/g instead of 19 m^2/g, obtained without "catalyst". Moreover, going to 40 *g* acceleration allowed us to produce a-Al_2O_3 powder of 72 m^2/g specific surface; in doing so the average crystallite size, ~20.3 nm, defined from X-ray line breadth is agrees well with the size calculated from the surface value by the formula: $D = 6\rho S$, that is 20.8 nm.

Contamination when grinding

It is possible that the most serious drawback of the power-intensive mills using for fine and superfine grinding of inorganic oxides should be considered the inevitable contamination of the matter, being ground, by the grinding media abrasion products and, to the less extent, by that of the rollers. To a first approximation, the contamination level increases much as t/r^2, where t is grinding time, and r is crystallite size of the oxide being ground. Hence, shown in Fig. 2 are the X-ray spectra of aluminum oxide, ground by steel and ceramic (ZrO_2 to be illustrative) balls in the corresponding rollers. 10 min of treatment under 20 *g* acceleration are yet enough for distinct three peaks showing out at the X-ray spectrum appropriate to monoclinic and cubic modifications of zirconium oxide, and 20 min treatment under 40 *g* acceleration by steel balls results in almost 20 % contamination.

Though by optimization of mechanic treatment conditions, and, in particular, by enhancing of grinding media quality, one can considerably reduce its abrasion (by a factor of ~10), solving cardinally the problem of pure

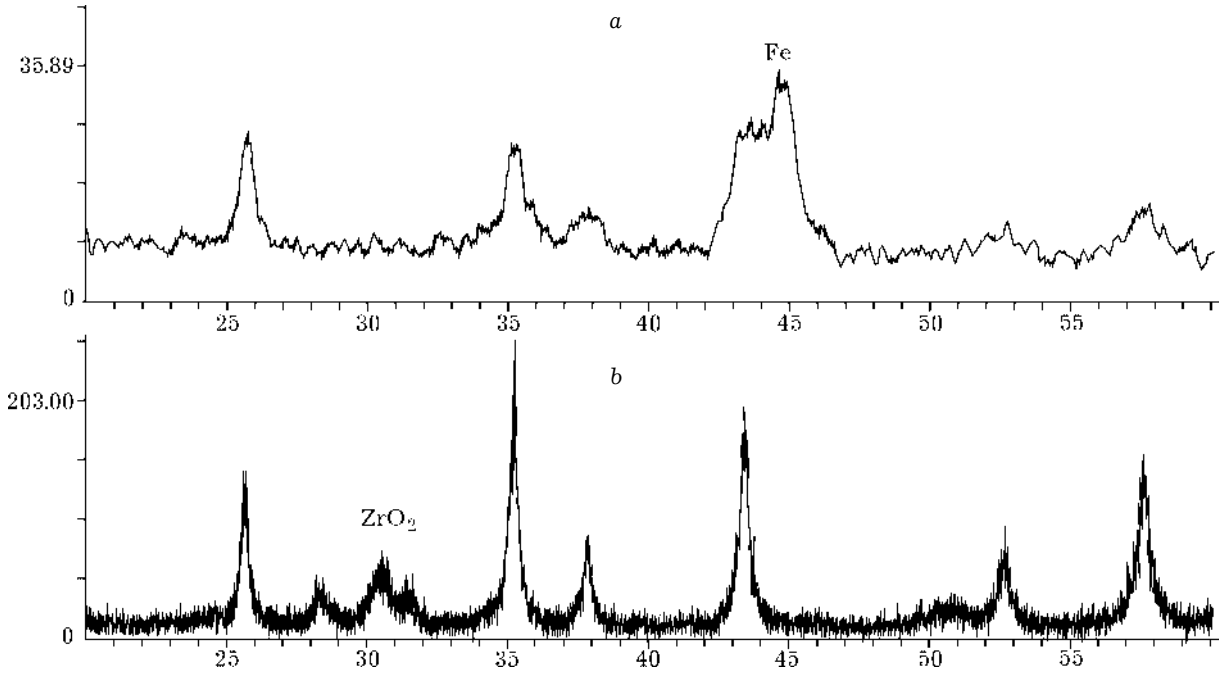

Fig. 2. X-ray spectra of mechanically treated a-Al_2O_3: *a* – 20 min, 40 *g*, steel balls; *b* – 10 min, 20 *g*, ZrO_2 balls. Marked reflexes are related to the substance of grinding media abrasion. *Y* axis units are arbitrary, and *X* axis units are 2q angles on all the diffraction spectra.

powder production in such a manner will apparently fail. This being so, the development of subsequent cleaning techniques for the ground down powder becomes urgent.

As we mentioned earlier [16], the prolonged boiling of the reduced powder in hydrochloric acid does not provide complete elimination of impurities. The remainder content of iron for the powder treated for 20 min under 40 *g* acceleration comprises 1.5 %, and content of chromium and silicon is about 0.5 %. It was indicated, that Mössbauer spectra identify Fe^{3+} ions in oxygen surround.

Additional investigations performed by EPR spectroscopy method confirmed unambiguously the assumption about Al_2O_3 – Fe_2O_3 solid solute formation under intense grinding. It is logical to assume that Cr is also incorporated in the crystal lattice of a-Al_2O_3. Hence, on aluminum oxide grinding in power-intensive planetary mills the following set of mechanochemical reactions takes place:

$$Fe + O_2\ (H_2O) \rightarrow Fe_2O_3$$

$$Fe + Fe_2O_3 \rightarrow Fe_3O_4,\ FeO$$

$$Al_2O_3 + Fe_3O_4,\ FeO \rightarrow Al_{2-x}Fe_xO_3$$

Presence of the two first reactions has been confirmed by special experiments. It was shown, that prolonged grinding of aluminum oxide (and other oxides) in hermetically closed roller brings about the great vacuity. On pricking the rubber gasket with the syringe filled with liquid, the liquid intake occurs. It would appear reasonable the oxygen consumption from the roller to form the iron oxide. Moreover, it turned out that 30 min of Fe_2O_3 grinding is enough for FeO reflexes alone in X-ray spectrum.

It is apparent that implementation of the grinding in inert media is bound to prevent the possibility of solid solute formation, and, seemingly, make it possible to achieve considerably less remainder content of iron and chromium through hydrochloric acid treatment.

For this purpose, loaded rollers supplied with special devices have been evacuated for a long time under heating (~200 °C), and then filled with Ar up to 2 atm. However, despite the multiple acid treatment, the remainder iron content turned out to be at a level of 10 mass %. The powder is of absolutely black colour and is readily attracted to the magnet. Though the crystallites size appeared to be at a level of 16 nm, its specific surface comprised nothing

more than 10 m^2/g. Let us notice, that under the same conditions, but in air media, the powder has been produced with the average crystallite size of 25 nm and with the specific surface of about 60 m^2/g.

Apparently, under conditions indicated, the tendency to aggregation is considerably more distinct. The compact aggregates hold the iron particles inside, so that they are beyond the reach of hydrochloric acid attack, and so we deal with the Fe – Al_2O_3 composite. It is quite possible that the difference between moisture content in the air and in argon plays a decisive role. With moisture present, the surface of the oxides, being treated, is covered with the hydroxide film, which may hinder the aggregate formation. It is possible also that absence of hydroxides would increase the friction coefficient between the treated particles and would allow to produce crystallites by a factor of 1.5 less in size, which are, clearly, more prone to aggregation in agreement with Fig. 1.

It becomes evident, that the solution of the problem to produce the least achievable in size and, at the same time, the most pure powder of a-Al_2O_3 through grinding is on the way of creating such conditions, which guard against any possibility of mechanochemical reactions with the abrasion products of grinding media and, simultaneously, prevent formation of the steady aggregates not subject to subsequent destruction. The best result achieved by us on this way is obtaining of a-Al_2O_3 powder with the average particle size of ~40 nm and iron content in purified sample ~0.02 %.

Let us also note, that initial coarse-dispersion aluminum oxide has 0.035 % iron content, *i. e.* we observed the effect of "mechanochemical purification" of powder. The effect seems to be rather reasonable one, when the possibility is taken into consideration to segregate the impurity atoms on the surface. Under superfine grinding, the multiple extension of the powder surface occurs, and rather high diffusion rate of atoms in particles under intensive plastic deformation results in prompt enrichment of the surface layer with the impurity. The subsequent acid treatment removes this highly defective and, even, amorphous-made surface layer.

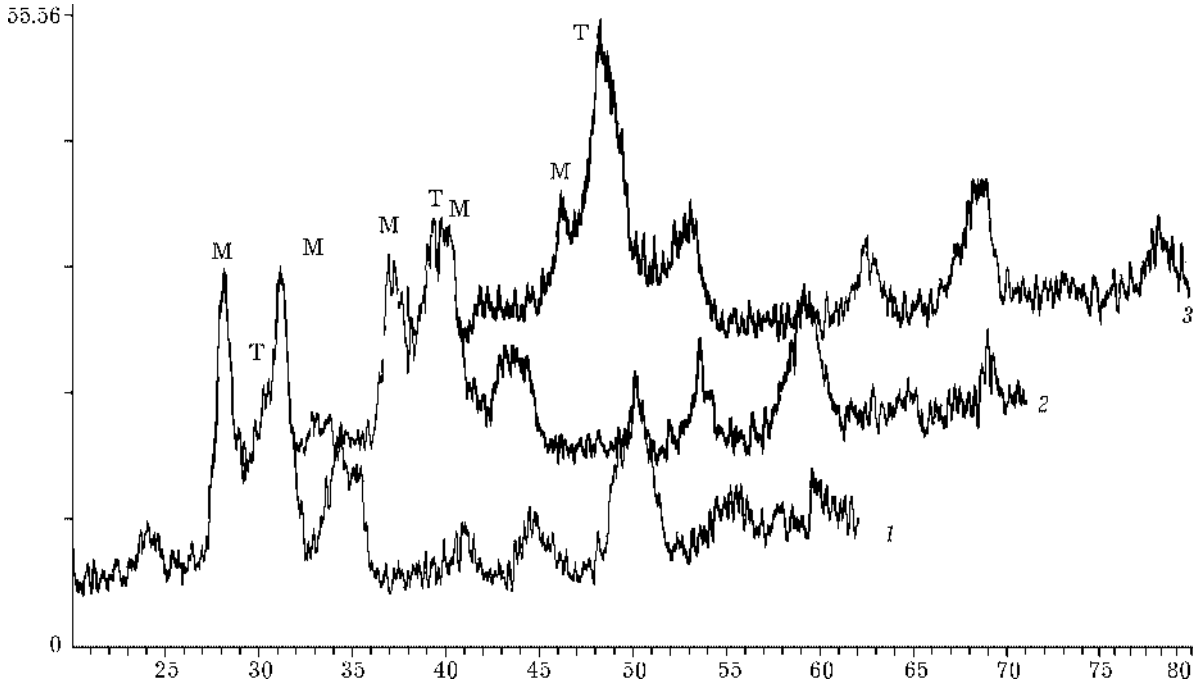

Fig. 3. X-ray spectra of mechanically treated ZrO_2 (40 *g*). *t*, min: 5 (*1*), 10 (*2*), and 15 (*3*). M – main reflexes of monoclinic modification, T – tetragonal.

Grinding of ZrO_2

Intensive mechanic treatment of zirconium dioxide is followed by phase transitions [18, 19], that, in authors' opinion, are due to the surface energy contribution in Gibbs potential. The increase of the oxide specific surface makes tetragonal or cubic modification of zirconium dioxide thermodynamically more stable, while for coarse-dispersion powder the stable phase is monoclinic.

In Figure 3 are shown the X-ray spectra of zirconium dioxide powder treated in the mill for varying time periods and initially made up of 100 % monoclinic modification, and in Fig. 4 are shown transformations that take place under subsequent thermal treatment of one of the samples. The relatively short mechanochemical activation under these circumstances is yet enough for more than 50 % phase transition of monoclinic modification into more symmetric one. Thermal treatment of the ground down samples initially leads to the increased extent of phase transition and causes the reversal transition under subsequent temperature rise.

Similar phenomena have been observed yet in the past, and in [18] they have been correlated with the crystallite size changes: with rise of the crystallite size a transition into monoclinic modification was evidenced and vice versa.

However, only through picturing the whole collection of the processes taking place under intensive mechanical treatment (see Fig. 1), one can get satisfactory explanation of the following experimental facts:

– mechanical treatment of tetragonal modification of ZrO_2 resulted in its prompt 100 % conversion to monoclinic modification [18];

– mechanical treatment of monoclinic modification, vice versa, results in its transition to tetragonal modification, the conversion extent under treatment by tungsten carbide balls being only 45 % [18] even after 50 h, whereas intense treatment by steel balls results in 100 % tetragonal modification in merely ~20 min [19];

– thermal treatment of mechanochemically synthesized tetragonal modification even at 800–900 °C converts it into monoclinic ([18], see Fig. 4), whereas we showed in special experiments, that voluminous sintering of the

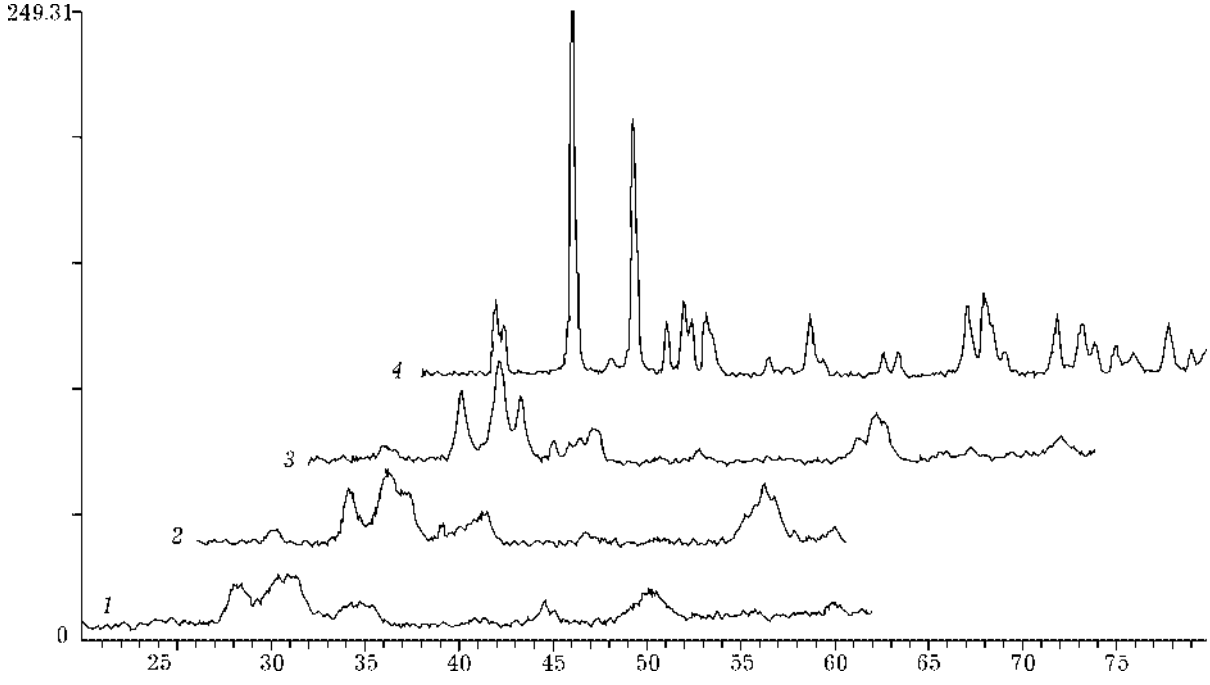

Fig. 4. X-ray spectra of mechanically treated ZrO_2 (40 *g*) for 10 min (*1*), then calcinated for 1 h (*2*, *3*) and 3 h (*4*) at 700 °C (*2*), 800 (*3*) and 900 °C (*4*).

sample made of zirconium dioxide mechanically ground in the planetary mill begins at temperatures higher than 1000–1050 °C.

In our opinion, these facts may have satisfactory explanation only under the assumption that intensive or prolonged mechanical treatment results in the state of dynamic equilibrium between the processes of crystallites lessening and their coalescence (minimum zone on the curve *1–3*, see Fig. 1). Crystallites with the size higher than critical one, and hence in the monoclinic phase, are being ground down and transit into more stable modification for the particles with the size less than the critical one. Reverse coalescence process for small particles gives rise to back phase transition. These two processes rates are equal in the state of dynamic equilibrium, and it is that why the attempt to obtain in [18] the extent of phase conversion more than 45 % failed.

Discrepancy with data, given by authors [19], is seeming. On intensive treatment by steel balls, there occur the substantial contamination by iron oxide, the oxidation of the latter one by air oxygen, and, most probably, formation of the mixed iron and zirconium oxide particles on the surface, this oxide separating ZrO_2 particles from each other and hindering their coalescence.

One may also suppose the ordinary stabilization of tetragonal modification by iron ions, much like the process when incorporating the ions of yttrium or calcium into zirconium dioxide. In this case, true enough, for explanation of reverse transition under heating, one is forced to admit also equalization of iron ions concentration within the sample under thermal treatment and its average value decrease (within the volume or on the surface) to the level below the stabilization barrier.

Experiments performed by us under conditions, which prevented the emergence of impurity compounds (ceramic balls and rollers), showed that in mere 10 min (acceleration 20 *g*) of mechanical treatment of ZrO_2 monoclinic modification the extent of phase conversion into tetragonal modification is about 30 %. The increase in treatment time up to 1 h or intensity change up to 40 *g* have practically no effect on that value.

It is also evident that, if highly dispersed tetragonal modification is mechanically treated, the process corresponds to the left side of curves *2* and *3* (see Fig. 1). Just slight mechanic action is bound to cause considerable crystallite growth and the accompanying it transition to monoclinic modification, which is fairly observed [18, 20].

Though the point corresponding to the zirconium dioxide being ground in Fig. 1 quickly reaches the curve *1–3* minimum on intensive mechanical treatment, its position on the curve *1–2* continues moving rightward to the area of more and more compact aggregates. This is

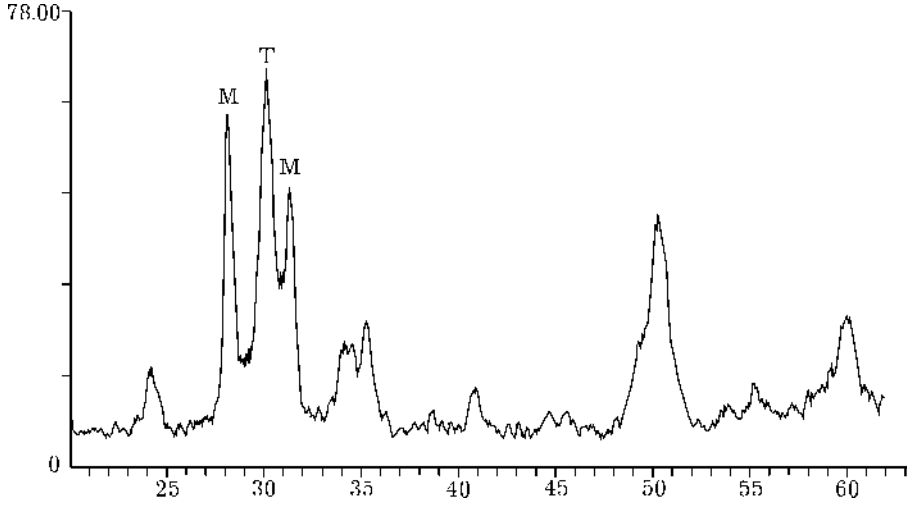

Fig. 5. X-ray spectra of mechanically treated mixture of ZrO_2 + 15 mass % Al (40 *g*, 10 min and calcinated at 1000 °C, 3 h).

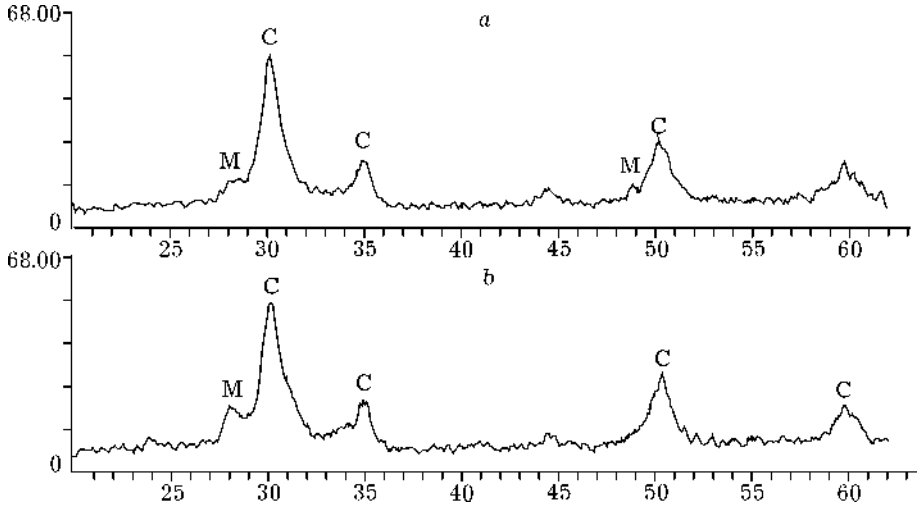

Fig. 6. X-ray spectra of mechanically treated (40 *g*, 15 min) mixture of ZrO_2 + 6 mol. % Y_2O_3 (*a*) and ZrO_2 +15 mol. % CaO (*b*).

evidenced, for example, by the values of crystallite sizes, given by authors [19] and determined from X-ray line breadths (that is 16 nm), and calculated from the specific surface values (49 nm).

Intensive sintering and grain growth in such aggregates is bound to start at the temperatures considerably lower, than the temperature of sample sintering throughout the volume. This is which accounts for the observable phase transfer in mechanically treated samples at the temperatures lower than the sintering one.

The experiment on ZrO_2 grinding with 15 % of metallic aluminum added serves as verification. Neither aluminum, nor its oxides do not interact with zirconium dioxide and hence one might expect that, having separated the particles of highly dispersed tetragonal modifications inside the aggregate, aluminum would prevent the crystallite growth and reverse phase transition under heating. Comparison of the phase composition beyond 900 ℃ (see Fig. 4) and beyond 1000 ℃ (Fig. 5) gives strong evidence, that aluminum does hinder the back transition into monoclinic modification, thus providing support for correctness of our view.

It is interesting to note, that the substance separating the crystallites from each other performs its function, even if it is present only at the stage of grinding. Thus, our substitution of aluminum by polyvinyl alcohol, which is, apparently, removed from the powder long before 800–900 ℃, also hinders transition to monoclinic modification on heating. It is evident, that crystallite growth in non-aggregated powder is possible only at the temperature higher than that of sintering initiation, *i. e.* higher than 1000 ℃.

From the above presentation it follows that generation of highly dispersed zirconium through simple intense grinding without implementation of specific techniques and "grinding catalysts" is impracticable. However, the same features of mechanochemical grinding mechanism, that hinder the nano-powder production, can be made use of with substantial positive effect.

A serious problem in ceramic articles production from ZrO_2 is the difficulty to obtain yttrium-stabilized or calcium-stabilized tetragonal or cubic modification. At the same time, it is evident that by adding yttrium or calcium compounds into mechanically treated zirconium oxide, it is practicable to produce the aggregated composite, in which very small ZrO_2 crystallites are separated by stabilizer (inter)-layers.

Shown in Fig. 6 are the results of these experiments. Based on these data, one cannot judge unambiguously, whether the formation of tetragonal modification is the result of nano-grinding with the added stabilizer acting as "catalyst", or the process proceeds further, and we deal with the product of mechanoche-

mical synthesis reaction. However, in either case, whether the stabilized zirconium oxide has been produced, or it is only the highly reactive precursor, it can be directly used in ceramics production. Sintered samples appear to be compact materials built of 100 % cubic ZrO_2 modification.

CONCLUSIONS

In our opinion, the experimental results presented above, obtained by us and cited ones, can be rather successfully interpreted within the frames of rather rough, and, as appeared, yet extremely productive scheme. The collection of processes, which take place on exposure of inorganic powders to intensive mechanical action in planetary, vibratory, ball and other mills, can be described in terms of dynamic equilibrium between the grinding of nanoparticles, comprising the powder, and their merging upon the exterior pressure applied. By monitoring this equilibrium through creation the barriers on the way of particle merging, or, on the contrary, through merging promotion, one can generate either nanocomposites, or the mechanochemical reaction products. The possibility of the further withdrawal of the barrier being provided in the first case, the production of rather highly dispersed powder can be achieved.

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