J Mater Sci (2007) 42:7964–7971
DOI 10.1007/s10853-006-1245-7

Role of metal additives in mechanochemical phase transformation of zirconia

Garegin R. Karagedov · Svetlana S. Shatskaya · Nikolai Z. Lyakhov

Received: 10 April 2006 / Accepted: 10 November 2006 / Published online: 30 May 2007

Abstract Reasons for a phase transition in zirconia subjected to intensive mechanical treatment in planetary mill have been considered. If steel balls and vials are used for milling the comminution is accompanied by oxidation of wear metal particles and successive mechanochemical reaction with ZrO_2. Aluminum has been shown to behave similarly and, being deliberately added to zirconia powder, to form solid solutions. Foreign metal cations introduced into the lattice stabilize a modification with higher crystal symmetry thus increasing the threshold size above which the monoclinic modification is stable. An increase of surface energy contribution to the Gibbs' energy of zirconia plays an important role in phase transformation at the initial stages of mechanical treatment, while henceforth thermodynamic stability is more and more determined by the stabilizing effect of the impurity cations. Under the conditions that rule out contamination of ZrO_2 with wear material or other metal additives, dynamic equilibrium sets in between the direct transition to the tetragonal phase and the reverse transition to the monoclinic form.

Introduction

An intensive mechanical treatment of solids particularly in mills of different kinds is frequently accompanied by phase transitions to modifications that are normally stable at high pressure and temperature [1–5]. This phenomenon is generally considered as being an evidence of the generation of high pressure and temperature pulses during a collision of a milling body with the material under treatment and quenching the state that is non-equilibrium under usual conditions.

Such a transition of the monoclinic modification of zirconia (m-ZrO_2) to the tetragonal one was reported in 1976 [6]; later it was observed by many researchers who used different experimental conditions [7–11]. The non-equilibrium character of the processes taking place in mills considered by the authors of [11] as the main reason of the observed phase transition, that is a traditional point of view among mechanochemists, while the authors of [6, 7] reported an increase in the specific surface area of the powder having been treated (and hence the increased contribution of the surface energy to the Gibbs energy) to be the determining factor. This assumption is based on the hypothesis [12] that the tetragonal modification of ZrO_2 (t-ZrO_2) has lower surface energy in comparison with the monoclinic form, which becomes unstable as the size of the crystallites decreases to a definite critical level.

There are dozens of publications on synthesis of fine powder of zirconia in a tetragonal and/or cubic modification but there still is a controversy on whether the formation of highly symmetrical phases is due to kinetic reasons or they are indeed stable thermodynamically due to their size [13]. It was shown [14] that a complete transition to the tetragonal modification occurs during the annealing of a nanocrystalline mixture of the tetragonal and monoclinic phases under conditions excluding growth of particles. This provided convincing evidence that the more symmetric modification is stable in the nanocrystalline state. Shortly afterwards the analysis [15] indicates that if the terms

---

G. R. Karagedov (✉) · S. S. Shatskaya · N. Z. Lyakhov
Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch, Russian Academy of Sciences, Kutateladze 18, Novosibirsk 630128, Russia
e-mail: garik@solid.nsc.ru

involving the surface energy and Laplace pressure are introduced into the formula for Gibbs energy, temperature of the phase transition from the monoclinic modification into tetragonal one appears to depend on reciprocal particle size, which was confirmed experimentally by the authors. Additionally, the critical particle size below which the tetragonal modification is stable was determined to be 22.6 nm, which is very close to the values obtained by various experimental methods [16–18]. Finally, after experimental determination of the excess enthalpies of nanocrystalline tetragonal, monoclinic and amorphous ZrO_2 followed by a conclusion that with increase in the surface per mole of oxide at first tetragonal modification should become stable, and then the amorphous one [19] it appears be proved that lower surface energy of more symmetrical phases of zirconia makes just them thermodynamically stable in the nanocrystalline state.

Thus the mechanically stimulated phase transition observed in ZrO_2 in different mills does not seem to be due to the non-equilibrium character of the processes. At the same time, experimental data obtained by vigorously grinding ZrO_2 are difficult to interpret from the viewpoint of the decreased size of particles as the major reason for the observed phase transition [10, 20]. The attention was drawn to the fact that, according to the model proposed and confirmed in [20], intensive mechanical grinding should result in the dynamic equilibrium state when the rates of comminution and fine crystallites coalescence become equal, leading to the equilibrium particle size of the material under treatment. This accounts for the situation observed in [6, 8]: the degree of phase transition reached approximately 40%, and then remained constant. At the same time, 100% tetragonal modification was derived within rather short time of milling in [7, 9, 10]. It should be noted that milling bodies and cylinders made of tungsten carbide were used in [6, 8] while [7, 9, 10] involved those made of steel. The iron admixture formed due to wear of the milling bodies has been supposed to participate in the phase transition under consideration [10, 20]. Either separation of ZrO_2 particles by the metal was assumed to prevent recrystallization similar to that reported in [21] or incorporation of iron cations into the oxide lattice accompanied by stabilization of tetragonal/cubic modifications (t/c-ZrO_2) was admitted.

The opinion proposed in [20] became even more urgent after the mechanochemical reactions $ZrO_2 + Fe_2O_3$ resulting in the formation of tetragonal solid solution containing up to 20 mol.% of ferric oxide were carried out as described in [8, 22], and it was shown in [23] that even 0.7% of iron introduced into amorphous zirconium hydroxide results in prevailing formation of the tetragonal modification upon heating, while 2 wt.% of the metal is sufficient for 100% stabilization of the latter modification.

The present work deals with a more detailed investigation of mechanically stimulated phase transition in ZrO_2 and the role of metal admixtures in this process.

Experimental procedure

Chemically pure (Kh. Ch. reagent grade) zirconium oxide powder was used in the present study. The X-ray phase analysis revealed well-crystallized monoclinic modification with the crystallite size more than 0.2–0.3 μm and no other phases detectable.

The X-ray diffraction investigation was carried out with DRON-4 diffractometer, CuK_{α}1 radiation with graphite monochromator at a rate of 0.25–0.5 °/min. Relative content of the phases and crystallite size were determined using Rietveld procedure with the help of Powdercell program. Verification which was carried out for specially prepared mixtures of aluminum and zirconium oxides showed that the accuracy of composition determination was at the level of 5 rel.%. Crystallite sizes were derived from all peaks within 20–80° (2Θ) interval. Sample of α-Al_2O_3 annealed at 1,600 °C was taken as a standard.

Mechanical treatment was carried out with AGO-2M planetary mill (Novic Co., Russia) with the acceleration within the range 15–40 *g*. Stainless steel balls (ShKh-15) and wear-resistant balls made of ZrO_2 (manufactured by TOSOH company) were used. The latter exhibited excellent wear resistance under conditions used with no detectable loss of weight for more than 500 min milling. In some experiments alumina balls and vials were used. Ball to powder mass ratio was 1:40, 1:33.5, and 1:38.5 for steel, zirconia, and alumina balls, respectively. Water or its mixture with ethylene glycol was used as a vial cooling liquid. The temperature of cooling liquid could be controlled from 0 up to 120 °C.

The iron/aluminum content of the samples was determined by means of flame photometry. The solutions obtained by treating the powder with hydrofluoric acid or aqua-regia were analyzed. In the first case the substance dissolved completely; in the second case only metal that did not enter the lattice was assumed to dissolve, since usual ZrO_2 is stable under the action of aqua-regia. The difference in the results of analyses was taken to correspond to the amount of iron having entered the dioxide lattice.

The samples were annealed for 1 h in a muffle furnace, with temperature maintained with an accuracy of 5° in the air or in a foil made of aluminum or stainless steel, depending on temperature. A small packet made of foil was placed on the bottom of a closed porcelain crucible under a thick layer of acetylene black preventing access of oxygen.

Results and discussion

Earlier, in [20] we have noted a dramatic consequence of switching off vial cooling water during milling of zirconia. Under certain experimental conditions ordinary observed phase transition into more symmetrical modification did not occur without cooling while it did occur with it. Further investigation lead to data presented in Fig. 1 as the dependence of the degree of phase transition (DPT), that is, the ratio of the amount of tetragonal/cubic modification to the total quantity of zirconia, on the indicated cooling temperature. It should be noted that the X-ray diffraction patterns of the samples after mechanical treatment are strongly broadened and do not allow unambiguous interpretation of the formed modification as a tetragonal or cubic one. We failed to take Raman spectra as well that is likely due to substantial distortion of crystal lattice after intensive milling. In spite of the fact that X-ray diffraction patterns unambiguously point to tetragonal phase (t-ZrO_2) after annealing at 900 °C, as can be seen from the splitting of the (200), (220) and (311) diffraction peaks (Figs. 3c, 6c), whether it is a result of line narrowing or phase transition remains obscure. Therefore, below the corresponding phase will be referred to as tetragonal/cubic (t/c-ZrO_2).

It turned out that the DPT achieved over a particular time interval increases with the temperature of the cooling liquid to a maximum and then decreases notably. Of significant importance is that the mean crystallite size of the t/c phase formed appeared to be independent of the transition degree and falls within the range 20–25 nm for milling with 10 mm balls, and within the range 10–15 nm when 5 mm balls are used. Moreover, at any temperature of the cooling liquid, the powder obtained with smaller balls and composed of smaller crystallites has not higher but substantially lower portion of the t/c modification.

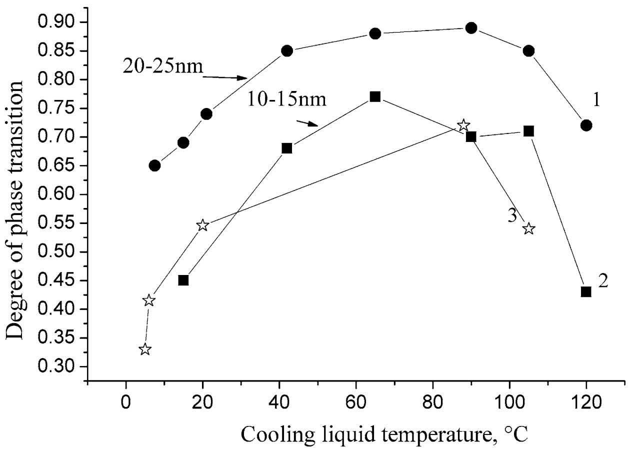

Fig. 1 The degree of transformation of the m-ZrO_2 into t/c-ZrO_2 after milling at 40 *g*, 15 min with 10 mm balls (1); with 5 mm balls (2), and at 20 *g*, 21 min with 10 mm balls (3) as a function of temperature of cooling liquid

Separate experiments with vials and balls of α-Al_2O_3 showed that the DPT achieves little more than 23%, though the mean crystallite size of the monoclinic phase (m-ZrO_2) decreases to 15–16 nm; this DPT is substantially lower than the values achieved with steel balls even with larger crystallite size.

When some ground samples heated in the absence of oxygen (Table 1, Fig. 2) the crystallite size grows up to 70 nm, which is well above all the theoretical and experimental estimations of the critical size above which the reverse transformation into the m-ZrO_2 should take place; however, this does not happen. The reversed transformation into the monoclinic modification occurs at 800 °C in an oxygen-free atmosphere and at 950 °C in the air and bears no relationship with the crystallite size. Clearly, the stability of t/c-ZrO_2 produced by intensive milling should have another explanation not related to the size.

Discussion of reasons for the complex dependence of the DPT on temperature of the cooling liquid is beyond the scope of the present paper. It is clear, however, that the above-presented results do not agree with the hypothesis that mechanically stimulated transition is due to a decrease in particle size. Evidently, if an increase in the contribution from the surface energy into Gibbs energy is of importance, it is not a sole factor determining the degree of phase transition.

In Table 2 are listed data of chemical analysis of iron content in some t/c-ZrO_2 powder produced under various experimental conditions. Taking into account the fact that after mechanical treatment zirconium dioxide becomes somewhat soluble in *aqua-regia* (up to 10–15%), iron content presented above may even have been slightly underestimated. It follows from these data that a substantial amount of ferric cations enter the ZrO_2 lattice and appears to stabilize the more symmetrical phase. According to [23], this amount of cations is sufficient to provide the observed transformation degree. The content of iron incorporated into the dioxide is higher for the higher energy of milling balls, which decreases along the row 40 *g*–10 mm, 20 *g*–10 mm, 40 *g*–5 mm. This is quite reasonable, because the rate of the assumed reaction of mechanochemical synthesis

$$(1-x)ZrO_2 + 0.5xFe_2O_3 \rightarrow Zr_{1-x}Fe_xO_{2-0.5x}$$

is determined by the intensity of plastic deformation and the volume within which deformation takes place under a single action of a ball.

It was assumed [8] that mechanochemical interaction of zirconium and iron oxides gives the cubic form (for the solid solution containing 5 mol.% Fe_2O_3, the lattice parameter was reported to be 5.093 Å). To compare our

Table 1 Crystallite size, DPT, and lattice parameters of milled zirconia annealed at different temperatures

Temperature (°C)	Crystallite size of t/c-ZrO_2 (nm)	DPT (%)	Lattice parameter (Å)
25	19	85	5.104
500	39	83	5.098
700	71	84	5.101
850		2.5	

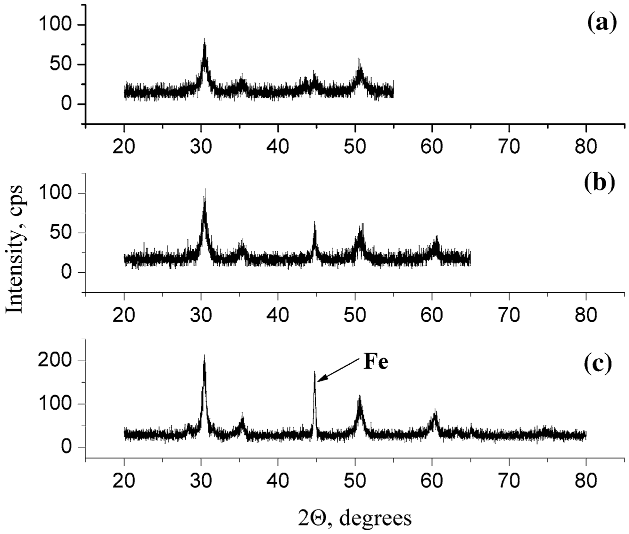

Fig. 2 Diffraction patterns of the ZrO_2 sample milled at acceleration 40 *g* for 15 min with 10 mm steel balls (**a**) and annealed in oxygen-free atmosphere at 500 °C (**b**) and 700 °C (**c**). Temperature of cooling liquid is 105 °C

Table 2 Fe_2O_3 content in ZrO_2 milled under various conditions

Acceleration (*g*)	Ball diameter (mm)	Temperature of cooling liquid (°C)	Milling time (min)	Fe_2O_3 content in lattice (mol.%)
40	10	25	25	4.5
40	10	42	15	6.0
40	10	>105	15	4.1
40	5	90	15	2.2
40	5	>105	15	1.0
20	10	88	21	3.1

results with the data of [8], we also performed calculations for the cubic cell (parameters listed in Table 1). The lattice parameter remains the same within the limit of 0.1 rel.% under thermal annealing and falls into the line with that calculated by the equation developed in [24] for the cubic zirconia with 3 mol.% Fe_2O_3, the latter being close to the iron content given in Table 2. These data provide evidence in favor of chemical reaction proceeding as a result of mechanical treatment and the formation of zirconium dioxide stabilized by ferric cations.

In addition to the peaks assigned to t-ZrO_2, the X-ray diffraction pattern of milled zirconia (Fig. 2a) indicates the presence of low carbon steel (martensite) and α-Fe at 2Θ equal to 43.4 and 44.7, respectively. During annealing in an oxygen free atmosphere, a narrow and intensive peak is formed within this angle range making possible to detect as low content of α-Fe phase as 1 wt.%. This circumstance becomes extremely important for the analysis of data presented in Fig. 3 showing the transformation of the X-ray diffraction patterns of the sample treated mechanically with steel balls till almost complete transition into t/c-ZrO_2, then subjected to hydrochloric acid leaching, and subsequent annealing in the air at 900 and 1,000 °C. At 900 °C, the diffraction patterns exhibit 100% tetragonal ZrO_2 and no other phase detectable, while at 1,000 °C phase transition into the m-ZrO_2 with simultaneous appearance of α-Fe_2O_3 (hematite) peaks occurs. These data are in good agreement with the results of electron diffraction investigation described in [22] for the mechanochemically synthesized solution containing 18 mol.% Fe_2O_3.

The amount of hematite which we estimated using Rietweld procedure to be 4.8 mol.% is in good agreement with the value 4.5% obtained by means of chemical analysis for the metal having entered the lattice, see Table 1. Only Fe^{3+} cations dissolved in the t-ZrO_2 (Fig. 3c) may

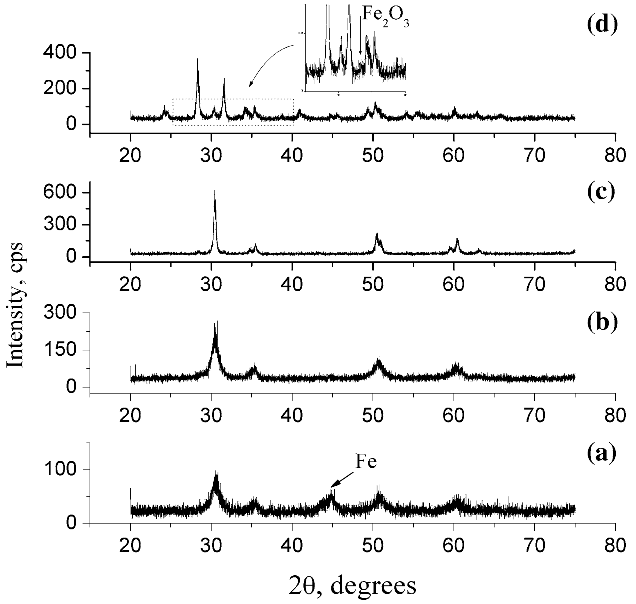

Fig. 3 Diffraction patterns of ZrO_2 milled with steel balls 10 mm in diameter with the acceleration of 40 *g* for 25 min (**a**), then washed with hydrochloric acid (**b**), then annealed in the air at 900 °C (**c**) and at 1,000 °C (**d**)

yield hematite on heating because washed with HCl and subsequently annealed in the absence of oxygen at 700 °C sample (not shown in the Fig. 3) does not contain any α-Fe phase and; thus, as we have already stressed above, the content of iron may be little more than 1%.

Thus it may be stated that ferric cations not only enter the lattice of zirconia but also stabilize its t/c modification just as yttrium, calcium, and some other cations do. When a sufficient mobility of the lattice elements is achieved, the solid solution which is metastable under these conditions gets decomposed, resulting in disappearance of the stabilizing effect of iron and the transformation of ZrO_2 into the monoclinic modification. A similar explanation of thermal decomposition of mechanochemically synthesized Ca and Mg–ZrO_2 has been reported in [25]. The fact that the solid solution stabilized with iron is metastable at this temperature is confirmed by much lower decomposition temperature in an atmosphere with low oxygen partial pressure, though it is known that, quite contrary, thermodynamic stability of t-ZrO_2 and solid solutions based on it rises under the lack of oxygen [26–28]. Decomposition takes place when the sufficient diffusion mobility of lattice elements is achieved, the mobility being certainly higher for higher concentration of the anion vacancies, which is provided by low oxygen pressure.

The set of the above-mentioned results provides evidence that high-energy milling of zirconium dioxide in a steel tool is accompanied by the oxidation of the worn metal followed by mechanochemical synthesis of the metastable solid solution $Zr_{1-x}Fe_xO_{2-0.5x}$.

Indeed, after 20 min mechanical treatment at the acceleration of 20 *g* in argon the DPT does drop markedly in comparison with the treatment in the air, 58 and 38%, respectively. It may be assumed that impossibility of the oxidation of the worn metal by atmospheric oxygen complicates mechanochemical synthesis.

At the same time, estimation of the total amount of iron oxide which can be formed and then enter the ZrO_2 lattice after complete consumption of oxygen, present in a sealed vial as the powder-adsorbed form, water and oxygen molecules in the gas phase gives a value of 2 mol.%. The amount of iron oxide that entered the lattice, as determined by means of chemical analysis, exceeds this amount in some cases 2–3 times. It is likely that an additional source of oxygen, responsible, incidentally, for the mechanochemical synthesis in argon, is zirconium dioxide itself, which admits large non-stoichiometry and therefore can render its oxygen atoms for the oxidation of iron.

Hence contamination of the ZrO_2 lattice cannot be avoided by simply removing moisture and air from the vial in the hope to prevent iron from oxidation. The use of steel milling bodies and vials always implies the risk of non-removable iron impurities entering the lattice.

We made an attempt to interfere with the reaction between iron and ZrO_2 by adding in the vial 10 wt.% of acetylene black. The latter was assumed to act by at least one of the following mechanisms: it would either act as oxygen absorbing agent or it would bind the iron into carbides, or it would simply separate iron and zirconia particles from each other. To make the results more unequivocal steel vials with tungsten carbide balls have been used in these experiments. It should intensify the reaction due to higher ball density and lower iron content at the same time. Whichever the mechanism of carbon black action would realize, we expected a notable decrease in the DPT; this is what we observed in experiments (Fig. 4). However, in our opinion, the most remarkable feature of evidence presented in Fig. 4 is the fact, that the addition of acetylene black after the first 10 min of milling does not stop the transition process as it does being added at the very beginning of mechanical treatment.

This provides important indication that the reaction of mechanochemical synthesis passes through the stage of fine particles aggregate formation and it is an aggregate in which the interaction between components proceeds at subsequent stages. The addition of acetylene black after the first 10 min of treatment now cannot exert any influence upon interaction inside the aggregate that has been already formed.

There is no reason, however, for one not to take advantage of the above mechanism responsible for the contamination of zirconia. If he deliberately changes an

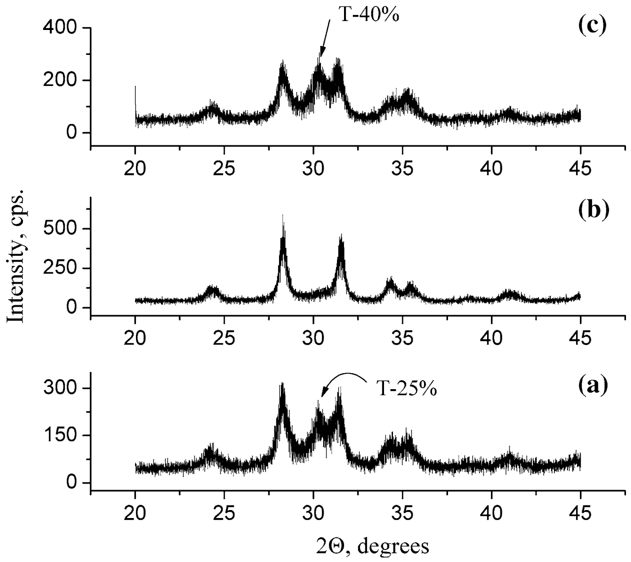

Fig. 4 Diffraction patterns of ZrO_2 milled with 10 mm tungsten carbide balls under the acceleration of 20 *g* for 10 min without adding carbon black (**a**), for 20 min with carbon black added (**b**), and with carbon black added at the second 10 min of grinding (**c**). Arrows indicate reflections corresponding to the t/c modification; its fraction is also indicated. T, t/c-ZrO_2

iron on any other metal he could obtain solid solution with the metal entered zirconia lattice. As an example we took aluminum which has been reported to form metastable stabilized solution with ZrO_2 [29–32] and has a higher than iron affinity to oxygen. Figure 5 compares the X-ray diffraction patterns of zirconia mechanically treated with 10 mm ZrO_2 balls in α-Al_2O_3 vials with and without addition of 5% Al metal. It is concluded that the former conditions are considerably more favorable (2.3 times) for the formation of t/c phase. Successive an hour annealing at 900 °C of the ZrO_2 samples proved to be even more conclusive because treated without Al powder underwent reverse transformation into m-ZrO_2 whereas the DPT of the other increased by a factor of 1.5.

We are forced to acknowledge that in our previous work [20] we erroneously interpreted preservation of the tetragonal structure of the product of intensive milling of zirconia with 15% Al after heating at 1,000 °C in air. It was assumed that aluminum separates zirconia particles during grinding, thus preventing their coalescence, and continues to do so after oxidation by heating. Further investigation (Fig. 6) showed that DPT achieved on grinding ZrO_2 with Al not only retains its value on successive heating in oxygen free atmosphere but also does drastically increase it. Most probably the phenomenon means that a considerable part of solid solution formed during milling exists in a highly disordered, may be even amorphous state and undergoes crystallization on heating, being crystallized in the metastable phase in the presence of tetragonal modification. Growth of zirconia nanocrystallites can hardly be effectively hindered by metallic aluminum well above its melting point and high temperature stability of tetragonal modification obtained is likely due to the stabilizing effect of Al^{3+} cations. An additional confirmation of this point is that X-ray pattern given on Fig. 6c corresponds to t-ZrO_2 mean crystallite size equal to 60 nm, while estimation of the pattern of as milled zirconia gives only about 10 nm.

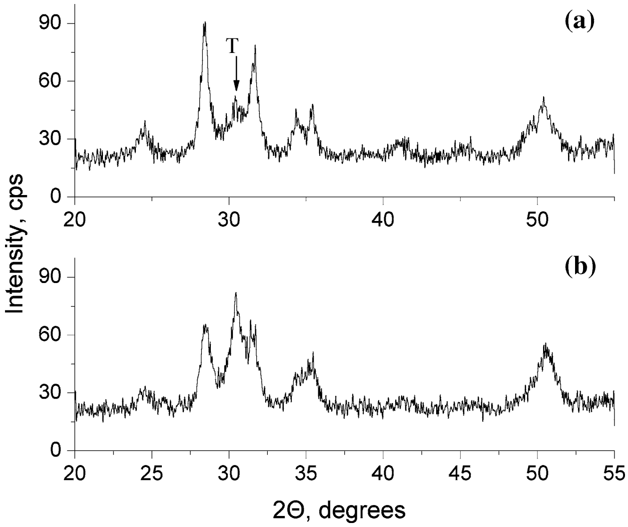

Fig. 5 X-ray diffraction patterns of ZrO_2 milled with 10 mm ZrO_2 balls in alumina vials without (**a**) and with (**b**) 5% aluminum additive at 20 *g* for 21 min. T,t/c-ZrO_2

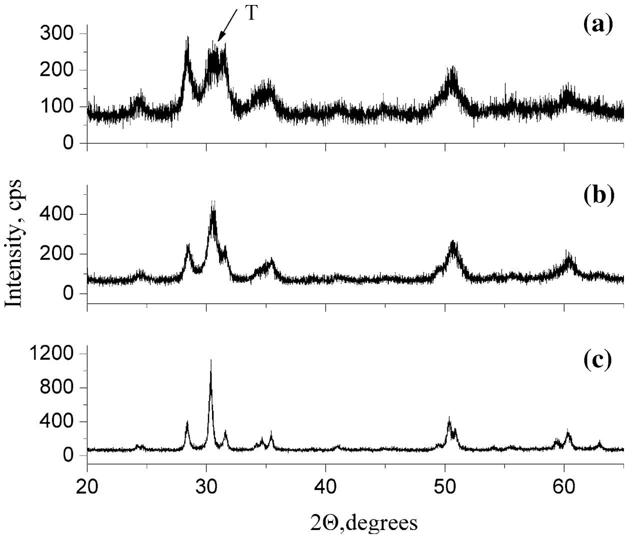

Fig. 6 X-ray diffraction patterns of 5 wt.%Al-ZrO_2 powder milled in steel vials with 5 mm zirconia balls at 20 *g*, 21 min and annealed over 1 h at 700 °C (**a**), 900 °C (**b**), and 1,050 °C (**c**). T, t/c-ZrO_2

The results of chemical analysis presented in Table 3 provide further support for the above considerations, that oxidation of aluminum similar to that of iron described earlier followed by mechanochemical interaction with ZrO_2 to form tetragonal/cubic solid solution. For understanding the mechanism as a whole, it is interesting that almost all Al enters the crystal lattice of zirconia during milling, so that the increased DPT on heating might indeed be due to crystallization of amorphous substance.

It should be stressed that, though the stabilizing effect of iron and/or aluminum cations substituting for zirconium in crystal lattice has been, in our opinion, established reliably we do failed to obtain a strict correlation between the DPT and the amount of foreign metal present in ZrO_2 estimated by chemical analysis.

Table 3 DPT and aluminum content in ZrO_2 milled at 25 *g*, 40 min with 3 wt.% of Al

Sample	DPT (%)	Content of Al determined in HCl extract (wt.%)	Content of Al determined by complete dissolution in HF (wt.%)
As ground	83	~0.1	2.6 ± 0.2
Ground and heated at 950 °C, 1 h	97	~0.1	2.6 ± 0.2

This means that the DPT in conditions allowing a foreign metal interfere in the process of intensive grinding is determined by the combined effect of the dimensional and chemical factors. Indeed, on Fig. 5a the formation of approximately 20% of tetragonal phase may be clearly detected even if no stabilizing cations are present in the vial. It appears that under intensive mechanical treatment in the mill, gradual increase in the fraction of particles with the size smaller than the critical value occurs. On the other hand, as the mechanochemical synthesis proceeds, the critical size itself increases similar to that described in [15] for the case of yttrium stabilized zirconia. Both factors promote the transition into the tetragonal/cubic modification and act simultaneously but perhaps to different extent at different stages of treatment.

The fact seems to be shown by investigating the effect of annealing on the kinetic curve of mechanically stimulated phase transition with the grinding balls made of ZrO_2 (Fig. 7). In this case, the amount of worn iron decreases sharply attaining no more than 2 wt.% within 20–25 min, which allows us to consider its effect insignificant for short treatment time. One can see an inflection after ~12.5 min of treatment, which becomes more distinct after annealing. The size of crystallites comprising the powder increases during heating, for example, from 16 to 40 nm and from 18 to 36 nm for the samples heated for 12.5 and 25 min, respectively.

For the samples obtained within short periods of time, growth of particles is accompanied by the reverse transformation of the t/c modification into monoclinic one, since at a short time of mechanical treatment the transition is caused by the dimensional effect. As treatment time increases, mechanochemical synthesis with iron, resulting in increased critical size of particles, becomes predominant. Because of this, the effect of thermal annealing on the stability of the t/c-ZrO_2 weakens; finally, treatment for 25 min is sufficient for keeping the t/c-ZrO_2 stable within the whole temperature range. During this time, about 2 wt.% of iron gets inserted into the lattice; this amount being sufficient for complete stabilization of the t/c-ZrO_2. Evidently, annealing at the decomposition temperature of the solid solution (1,000 °C) causes a complete transition to the initial state.

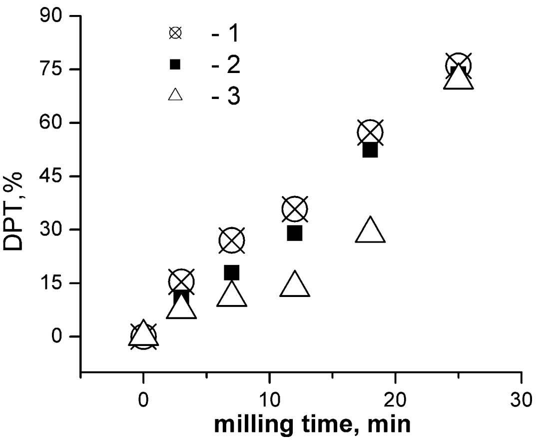

Fig. 7 The degree of transformation of m-ZrO_2 into t/c-ZrO_2 during mechanical treatment with 10 mm ZrO_2 balls at 25 *g*, depending on time of treatment (1), followed by annealing at 800 °C (2) and at 900 °C (3)

So, the observed phase transition is a result of two parallel processes differing in their kinetic features. Particles start to decrease immediately, while the mechanochemical synthesis reaction requires induction period due to the necessity for iron to get worn, oxidized, and to form aggregates with fine zirconia particles. If no special measures are taken to prevent crystallites coalescence, comminution alone leads to the achievement of mechanochemical equilibrium according to the model described in [20], and therefore only partial transition into the phase of higher symmetry can be achieved, in full agreement with the data presented in [6, 8].

Conclusions

Under intensive mechanical treatment of ZrO_2 in a steel vial and/or a steel milling body, as well as with deliberately fed metal additive, phase transition from the monoclinic modification to the more symmetrical one occurs; the degree of this transformation being determined by the intensity and time of treatment.

The phase transition is due to two parallel processes. At the initial stage, a decrease in particle size largely contributes to transformation. As the process develops, stabilization of tetragonal/cubic modification by metal cations entering the lattice becomes increasingly important. When ZrO_2 is treated under conditions excluding the presence of a metal, the transition degree decreases substantially reaching a limit when the rates of grinding and coalescence become equal and the system comes to the dynamic equilibrium state.

The tetragonal/cubic modification formed is thermally unstable and is transformed into the monoclinic one during heating. The upper temperature of the stability of symmetrical phase is determined by the partial pressure of oxygen and amount as well as nature of the stabilizing metal in crystal lattice.

Al_2O_3–ZrO_2 tetragonal solid solutions stable up to 1,100 °C have been synthesized mechanochemically.

References

1. Avvakumov EG (1986) Mechanokhimicheskie metodi aktivatzii khimicheskikh prozessov. Nauka, Novosibirsk

2. Heinicke G (1984) Tribochemistry. Akademie-Verlag, Berlin
3. Suryanarayana C (2001) Prog Mater Sci 46:1
4. Gaffet E, Bernard F, Niepce J-C, Charlot F, Gras C, Le Caer G, Guichard J-L, Delcroix P, Mocellin A, Tillement O (1999) J Mater Chem 9:305
5. Boldyrev VV, Tkacova K (2000) J Mater Synth Proc 8:121
6. Bayley JE, Lewis D, Librant ZM, Porter LJ (1972) Trans J Brit Ceram Soc 71:25
7. Qi M, Fecht HJ (1998) Mater Sci Forum 269–272:187
8. Jiang JZ, Poulsen FW, Morup S (1999) J Mater Res 14:1343
9. Kuznetsov PN, Kuznetsova LI, Zhizhaev AM (2002) Chem Sustain Dev 1–2:89
10. Karagedov GR, Ryzhikov EA, Shatskaya SS (2002) Chem Sustain Dev 1–2:47
11. Stubicar N, Bermanec V, Stubicar M, Popovic D, Kaysser WA (2004) J Alloys Compd 379:216
12. Garvie RC (1965) J Phys Chem 69:1238
13. Suresh A, Mayo MJ, Porter WD, Rawn CJ (2003) J Am Ceram Soc 86:360
14. Wu N-L, Wu T-F, Rusakova IA (2001) J Mater Res 16:666
15. Mayo MJ, Suresh A, Porter WD (2003) Rev Adv Mater Sci 5:100
16. Garvie RC (1978) J Phys Chem 82:218
17. Chraska T, King AH, Berndt CC (2000) Mater Sci Eng A286:169
18. Durado E, Bouvier P, Lucazeau G (2000) J Solid State Chem 149:399
19. Pitcher MW, Ushakov SV, Navrotsky A (2005) J Am Ceram Soc 88(1):160
20. Karagedov GR, Lyakhov NZ (2003) KONA Powder Part 21:76
21. Karagedov GR, Lyakhov NZ (1999) NanoStruct Mater 11:559
22. Cao W, Tan OK, Zhu W, Jiang B (2000) J Solid State Chem 155:320
23. Kuznetsov PN, Kuznetsova LI, Zhyzhaev AM, Pashkov GL, Boldyrev VV (2003) Chem Sustain Dev 4:611
24. Kim D-J (1989) J Am Ceram Soc 72:1415
25. Michel D, Faudot F, Gaffet E, Mazerolles L (1993) J Am Ceram Soc 76:2884
26. Collins DE, Kirk A, Bowman RK (1995) J Eur Ceram Soc 15:1119
27. Lee J, Li H, Lee WY (2003) J Am Ceram Soc 86:2031
28. Zhu WZ, Yan M (1997) J Mater Sci Lett 16:1540
29. Balmer ML, Lange FF, Levi CG (1994) J Am Ceram Soc 77:2069
30. Ishida K, Hirota K, Yamaguchi O, Kume H, Inamura S, Miyamoto H (1994) J Am Ceram Soc 77:1391
31. Moreau S, Gervas M, Douy A (1997) Solid State Ionics 101–103:625
32. Srdic VV, Winterer M, Miehe G, Hahn H (1999) Nanostruct Mater 12:95