MECHANOCHEMISTRY AND MECHANICAL ALLOYING 2003

JOURNAL OF MATERIALS SCIENCE **39** (2004) 5181–5184

Features of the procedures to obtain ultrafine zirconium dioxide by mechanochemical method

E. G. AVVAKUMOV*, L. G. KARAKCHIEV
Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch,
Russian Academy of Sciences, Kutateladze str. 18, 630128 Novosibirsk, Russia
E-mail: avvakumov@solid.nsc.ru

The results of investigation of mechanochemical reactions in the mixtures of hydroxides and carbonates of alkaline and alkaline earth metals with zirconium oxychloride and oxynitrate are presented. It is shown that one of the features of interaction between the components is the formation of the salts of alkaline and alkaline earth metals along with X-ray amorphous zirconium-containing compound. It is demonstrated that the mechanical activation of the mixture of yttrium carbonate and zirconium oxynitrate, followed by thermal treatment of this mechanically activated mixture, results in the formation of solid solution ZrO_2-Y_2O_3 in cubic modification. © *2004 Kluwer Academic Publishers*

1. Introduction

Nanodispersed powder of zirconium dioxide is a metastable tetragonal modification, which is converted into the stable monoclinic modification at a temperature above 600°C. The tetragonal and cubic modifications can be stabilized by adding polyvalent metal cations, like Ca^{2+}, Y^{3+}, etc. [1]. These modifications are the most interesting materials that have won wide application in different areas of science and technology. Therefore, search for new ecologically safe methods of the preparation of nanodispersed zirconium dioxide in tetragonal and cubic forms is important for practice.

Nanodispersed particles of zirconium dioxide were obtained in tetragonal modification by mechanical activation of amorphous zirconium hydroxide without subsequent thermal treatment [2, 3]. Both tetragonal and monoclinic modifications are observed in activated products.

A new approach to the mechanochemical synthesis of inorganic compounds, which has been developed only recently, is based on mechanical activation of mixtures of solid acids, bases, hydrated compounds, basic and acidic salts, etc. The method was called soft mechanochemical synthesis [4, 5].

It has been demonstrated that suitably designed mechanochemical processing can be used to synthesize nanocrystalline particles dispersed within a soluble salt matrix [6]. Selective removal of the matrix phase by washing with appropriate solvents can yield nanoparticles of the desired phase as small as 5 nm [7].

The synthesis of ultrafine zirconia powders by mechanochemical reaction of $ZrCl_4$ with CaO has been investigated by means of X-ray diffraction, transmission electron microscopy, differential scanning calorimeter measurements [8]. Mechanical milling resulted in a nano-scale mixture of CaO and amorphous $ZrCl_4$, no evidence of any reaction was observed. Subsequent thermal treatment at temperatures above 300°C resulted in the formation of separate particles of tetragonal and cubic ZrO_2, 5–10 nm in diameter within $CaCl_2$ matrix.

The results of the investigation into the influence of the process variables on mean particle and crystallite size of ZrO_2 powders synthesized by mechanically activated reaction of anhydrous $ZrCl_4$ with MgO and Li_2O as exchange reagents are presented in [9]. The average particle and crystallite size of the ZrO_2 powder formed in the first system was affected by only the duration of milling (5 nm for 6 h); on the contrary, mean particle and crystallite size in the second reaction system depends both on milling time and the presence of inert LiCl diluent.

It was also shown that the cubic ZrO_2-Y_2O_3 solid solution with particle size of 100 nm can be obtained by mechanical activation of a mixture of zirconium oxynitrate and yttrium nitrate followed by thermal treatment at 1100–1300°C [10].

The goal of the present contribution is the investigation of chemical reactions of zirconium salts with the compounds of alkali and alkali earth metals under the conditions of mechanical activation followed by thermal treatment at 150–1200°C.

2. Experimental procedure

Commercially available hydrated oxides and salts of zirconium, calcium, yttrium, sodium were used as initial reagents. Mechanical activation of the mixtures of reagents was carried out in a laboratory planetary mill using titanium carbonitride balls (8 mm in diameter)

---

*Author to whom all correspondence should be addressed.

and zirconium jars [11]. The frequency of the rotation of jars around the common axis was 700 revolutions per minute, activation time was 5 min. Thermal treatment was carried out at different temperatures (150–1200°C) but the treatment time was kept constant (4 h).

The structures of products were determined by means of X-ray diffraction analysis with DRON-3M diffractometer using filtered Cu-K_α radiation. The size of crystallites was determined from the changes in half-widths of X-ray diffraction lines. Thermal analysis experiments were carried out using a S-1000 MOM derivatograph.

3. Results and discussion

In accordance with goal of the work, we studied the following reactions under mechanical activation and thermal treatment:

1. Decomposition of activated $ZrOCl_2{\cdot}8H_2O$;
2. $ZrOCl_2{\cdot}8H_2O + 2NaOH$;
3. $ZrOCl_2{\cdot}8H_2O + Ca(OH)_2$;
4. $3ZrOCl_2{\cdot}8H_2O + Y_2(CO_3)_3{\cdot}3H_2O$;
5. $ZrO(NO_3)_2{\cdot}2H_2O + Na_2CO_3$;
6. $3ZrO(NO_3)_2{\cdot}2H_2O + Y_2(CO_3)_3{\cdot}3H_2O$.

With the help of these reactions, it is possible to observe the influence of the nature of zirconium salts and the compounds of alkali and alkali earth metals (charge and cation radius and type of anion) on phase transitions in ZrO_2.

The summarized data on phase transformation and sizes of primary particles, depending on temperature, are presented in Figs 1 and 2.

The crystal lattice of $ZrOCl_2{\cdot}8H_2O$ is destroyed, and two H_2O molecules are released during activation for 5 min. According to the XRD, only pure tetragonal modification of ZrO_2 is observed after thermal treatment at 450°C; monoclinic modification occurs at temperatures higher than this point, and both modifications coexist simultaneously (600–900°C), but at 1200°C only monoclinic modification is observed. The particles size is equal to 16–17 nm for the tetragonal modification and 17–60 nm for the monoclinic modification within temperature range 450–600°C.

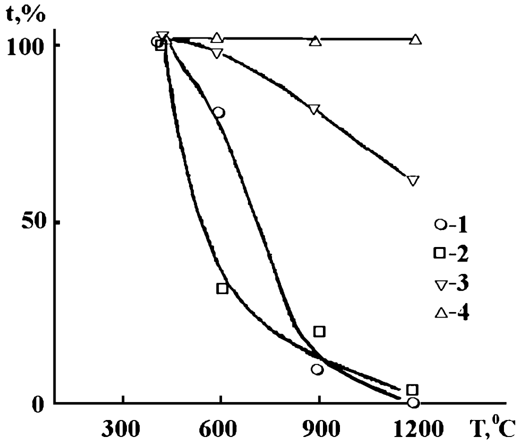

Figure 1 The content of ZrO_2 tetragonal modification (%) versus temperature of thermal treatment. Numbers correspond to reactions 1, 2, 3, 4 (see text).

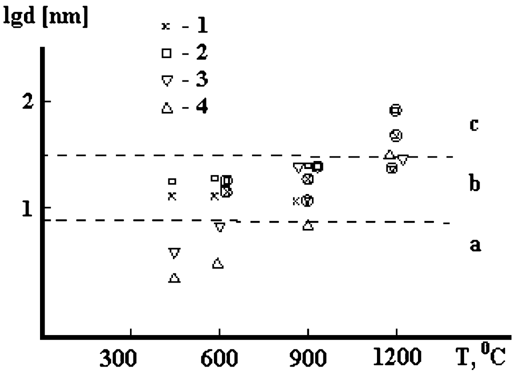

Figure 2 Log plot of the grain size (d, nm) vs. calcination temperature. Numbers correspond to reactions 1, 2, 3, 4. Phase field notation: (a) ZrO_2(T), (b) ZrO_2(T) + ZrO_2(M), and (c) ZrO_2(M). ZrO_2(M) grains are circled.

The reflections of sodium chloride in diffraction patterns have been detected after mechanical activation of a mixture of oxychloride with sodium hydroxide for 5 min. The sodium chloride plays the role of a matrix, which protects ZrO_2 particles from coalescence and is easily separated by dissolving in water. The size of ZrO_2 particles, which are the mixture of monoclinic and tetragonal modifications, increases from 24 to 31 nm in the temperature range 450–900°C, the size of the ZrO_2 of monoclinic modification increases from 21 to 85 nm in the temperature range 600–1200°C. Based on the DTA and X-ray data, it is possible to represent the scenario of transformations during activation and subsequent thermal processing by the following scheme:

$$\begin{aligned}
&ZrOCl_2{\cdot}8H_2O + 2NaOH\\
&\quad\xrightarrow{\text{activation}} 2NaCl + ZrO(OH)_2{\cdot}(8 - n) + nH_2O\\
&\quad\xrightarrow{25-230^\circ C} 2NaCl + ZrO(OH)_2 + (8 - n)H_2O\\
&\quad\xrightarrow{230-560^\circ C} 2NaCl + ZrO_2(T) + H_2O\\
&\quad\xrightarrow{560-900^\circ C} (2 - x)NaCl + ZrO_2(T) + ZrO_2(M)\\
&\quad\xrightarrow{900-1200^\circ C} ZrO_2(M) + NaCl\,(\text{traces}).
\end{aligned}$$

Chemical interaction in the mixture of zirconium oxychloride and calcium hydroxide has essential peculiarities. Calcium chloride is not observed in the XRD patterns of reaction products, but thermal analysis shows the appearance of a peak at 740°C corresponding to the melting point of calcium chloride. Tetragonal zirconia appears in samples calcined at 450°C. The grain size is about 5 nm at 450°C and 8 nm at 600°C. Monoclinic zirconia appears only in the samples calcined at 900°C, but even at 1200°C tetragonal zirconia is predominant in the sample. The grain size is 27 and 30 nm at 900 and 1200°C, respectively. The enhanced durability of the tetragonal phase in this case can be explained by partial incorporation of calcium into the zirconia structure.

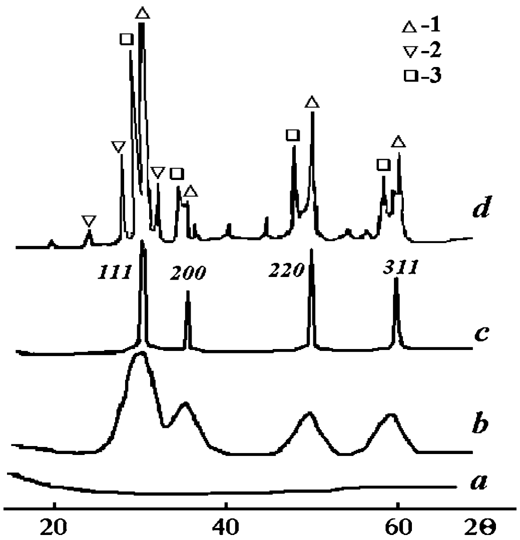

Figure 3 X-ray diffraction patterns of the $3ZrO(NO_3)_2{\cdot}2H_2O + Y_2(CO_3)_3{\cdot}3H_2O$ mixture: (a) activated mixture; (b) the same mixture thermally processed at 450°C; (c) the same at 1200°C, (d) separately activated, mixed and calcined at 1200°C. 1—ZrO_2(T), 2—ZrO_2(M), 3—Y_2O_3.

A solid solution of CaO in ZrO_2 is likely formed during activation and subsequent thermal processing. Another feature of this system is the fact that the monoclinic phase has a grain size (15 and 25 nm at 900 and 1200°C, respectively) smaller than the grain size of tetragonal phase observed under these conditions.

Activated $3ZrOCl_2{\cdot}8H_2O + Y_2(CO_3)_3{\cdot}3H_2O$ mixture is X-ray amorphous up to 320°C inclusive. Tetragonal zirconia appears after calcination at 450°C and is conserved without converting to monoclinic phase up to 1200°C inclusive. The grain size within temperature range 450–900°C increases from 3 to 8 nm and rises sharply to 35 nm at 1200°C. The stabilization of tetragonal phase can be explained by the formation of ZrO_2-Y_2O_3 solid solution.

The product formed after mechanical activation of $3ZrO(NO_3)_2{\cdot}2H_2O + Y_2(CO_3)_3{\cdot}3H_2O$ mixture is X-ray amorphous. The X-ray data are shown in Fig. 3. The joint activation is the necessary condition for the formation of cubic solid solutions of ZrO_2-Y_2O_3. Separate activation does not result in the formation of ZrO_2-Y_2O_3 solid solution.

An increase in temperature of the indicated mixture is accompanied by an increase in primary particle sizes. The reflections are narrowed at 1200°C, which allows us to determine the lattice parameter **a** of ZrO_2-Y_2O_3 solid solutions. As one can see from Fig. 4, an increase in yttrium content practically leads to the linear growth of the lattice constant **a**.

We suggested that chemical interaction proceeds in this mixture by the exchange reaction. The reflections of $Y_2(NO_3)_3$ are absent from XRD patterns of samples. In order to prove this suggestion, we have chosen a similar mixture: $ZrO(NO_3)_2{\cdot}2H_2O + Na_2CO_3$; the reflections of $NaNO_3$ were observed in the XRD patterns of mechanically activated mixtures. Thus, on the basis of the results obtained by X-ray and DTA methods, the following scheme of transformations during mechanical activation and thermal treatment can be suggested:

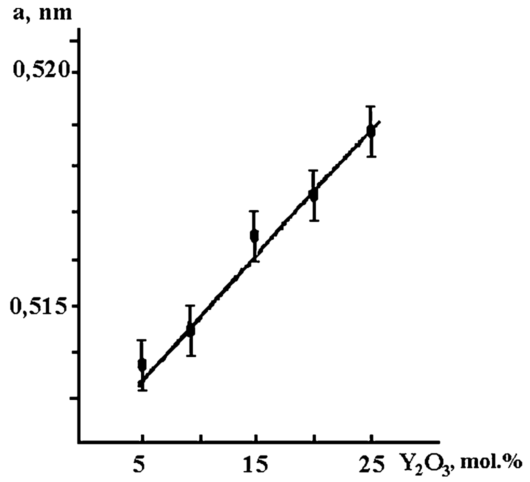

Figure 4 The lattice parameter **a** vs. composition of cubic solid solution of ZrO_2-Y_2O_3 prepared by calcination of the mechanically activated $3ZrO(NO_3)_2{\cdot}2H_2O + Y_2(CO_3)_3{\cdot}3H_2O$ mixture at 1200°C.

$$\begin{aligned}
&3ZrO(NO_3)_2{\cdot}2H_2O + Y_2(CO_3)_3{\cdot}3H_2O\\
&\xrightarrow{\text{activation}} 3ZrO(CO_3){\cdot}xH_2O + 2Y(NO_3)_3 \cdot yH_2O\\
&\qquad + (9 - x - y)H_2O\\
&\xrightarrow{25-500^\circ} 3ZrO_2\text{-}Y_2O_3 \text{ (solid solution)}\\
&\qquad + 3CO_2 + 9H_2O + 6HNO_3.
\end{aligned}$$

The data obtained by chemical analysis of the content of soluble yttrium compound ($Y_2(NO_3)_3$) in mechanically activated mixture and the ZrO_2-Y_2O_3 lattice parameter **a** vs. temperature of thermal treatment of the mixture are shown in Fig. 5. During thermal treatment at temperatures above 350°C, the content of yttrium nitrate decreases by the formation of ZrO_2-Y_2O_3 solid solution which is insoluble in water. The grain size of tetragonal zirconia depends on the composition of the system; for yttrium content from 5 to 25% mol., grain size decreases from 10.7 to 3.0 nm in the samples calcined at 450°C.

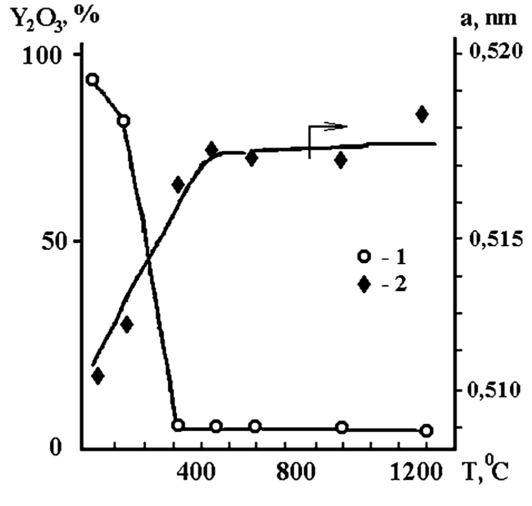

Figure 5 The content of soluble yttrium compound (% Y_2O_3) in the activated $3ZrO(NO_3)_2{\cdot}2H_2O + Y_2(CO_3)_3{\cdot}3H_2O$ mixture (1) annealed at different temperatures, and lattice parameter **a** (2) in washed samples (after thermal treatment at 1200°C).

4. Conclusion

It is shown that chemical interaction with the formation of thermally unstable products occurs during mechanical activation of the indicated mixtures. Thermal treatment of the intermediates results in the formation of nanodispersed ZrO_2 particles. The possibility of the formation of zirconium dioxide particles stabilized by Y_2O_3 in the cubic modification, which is stable under heating up to 1200°C, in mechanochemical reactions of hydroxides or carbonates of metals with zirconium oxychloride or oxynitrate is demonstrated.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research, project 02-03-33298.

References

1. V. N. STREKALOVSKY, YU. M. POLEZHAEV and S. F. PALGUEV, “Oxides with Admixed Disorder: Composition, Structure, Phase Transformations” (Nauka, Moscow, 1987) p. 160.
2. T. ISOBE and M. SENNA, *Sibirsky Khimichesky Zhurnal (Sib. Chem. J.)* **5** (1991) 25.
3. P. N. KUZNETSOV, A. M. ZHIZHAEV and L. J. KUZNETSOVA, *Zhurnal prikladnoi Khimii (J. Appl. Chem.)* **75** (2002) 177.
4. E. AVVAKUMOV, M. SENNA and N. KOSOVA, “Soft Mechanochemical Synthesis: A Basis for New Chemical Technologies” (Kluwer Academic Publishers, Boston/Dordrecht/London, 2001) p. 207.
5. M. SENNA, *Solid State Ionics* **63–65** (1993) 3.
6. J. DING, W. F. MIAO, P. G. MCCORMICK and P. STREET, *Appl. Phys. Lett.* **67** (1995) 3804.
7. J. DING, T. TSUZUKI and P. G. MCCORMICK, *J. Mater. Sci.* **34** (1999) 5293.
8. *Idem.*, *Nanostruct. Mater.* **8** (1997) 75.
9. A. C. DODD and P. G. MCCORMICK, *J. Metast. Nanocryst. Mater.* **15/16** (2003) 545.
10. L. V. MOROZOVA, T. J. PANOVA, A. E. LAPSHIN and V. B. GLUSCHKOVA, *Inorg. Mater. (Russia)* **36** (2000) 1001.
11. E. G. AVVAKUMOV, A. R. POTKIN and O. I. SAMARIN, Patent RU 975068, 1982.

Received 11 September 2003
and accepted 27 February 2004