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Low-Temperature Method of Synthesis of Nanopowder for the Production of Dense Ceramics Composed of ZrO_2 –8 mol. % Y_2O_3

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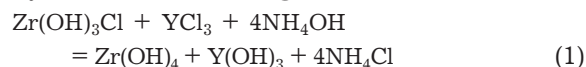
Abstract

Possibility of the low-temperature synthesis of zirconium dioxide nanopowder stabilized with yttrium (8 mol. %) from a mixture of hydrated zirconium oxynitride and yttrium carbonate mechanically activated in a continuous-type mill. It was shown that the powder formed even at 600 °C is easily moulded by dry pressing after disaggregation; its density after sintering is close to the theoretical value.

Key words: zirconium dioxide, synthesis, sintering

INTRODUCTION

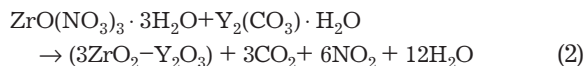
Zirconium dioxide relates to fireproof chemically stable materials and is widely used in the production of technical ceramics. To avoid fracturing of annealed hardware, which occurs due to the phase transition of the tetragonal modification of zirconium dioxide into the monoclinic one under cooling, its stabilization with metal oxides (Y^{3+} , Ca^{2+} , Mg^{2+} , Fe^{3+} etc.) is carried out. Insertion of stabilizing cations into zirconium oxide lattice occurs due to diffusion processes at sufficiently high temperatures. However, homogenisation of the system can be performed also in softer conditions using coprecipitation from solutions. To obtain yttrium-stabilized zirconium dioxide, which is widely used in practice, zirconium and yttrium are coprecipitated in the form of hydroxides that are formed during hydrolysis of a mixture of salts by ammonia according to reaction



The precipitate after its ageing is separated by filtering, dried and annealed at temperatures below 1000 °C [1]. However, this method has some complications, namely the use of

large volumes of solutions, the necessity to filter them, and consequent inevitable loss of reagents, as well as the use of ammonia solutions which requires special protection measures.

The mechanochemical method is considered today as an essential alternative to the widely used thermal synthesis because it allows a substantial decrease in energy consumption for the synthesis of the materials. It may be used to accelerate the processes of chemical interaction and to activate materials for sintering, which is the final stage in the industrial process of obtaining ceramic hardware for many purposes. To obtain zirconium dioxide, the soft mechanochemical synthesis is promising. This method is based on the use of mixtures of solid hydroxides and acids, hydrated oxides, basic and acidic salts, crystal hydrates as initial compounds to be loaded into the mechanochemical activator. This allows one to decrease the level of mechanical load substantially and to use less powerful grinding activators than those used for treating metal oxides. It was shown that after mechanochemical treatment of a mixture of reagents, as a result of reaction,



it is possible to obtain amorphous product; heating it at a temperature of 450 °C causes the formation of the crystalline solid solution $\text{ZrO}_2\text{-Y}_2\text{O}_3$ [2]. Nevertheless, the practical application of these results is likely to be possible only in the case if highly productive flow activator mills are used. This aspect may be studied using recently designed centrifugal mill with continuous performance in the vertical version providing the sufficient mechanical energy input per unit mass of the substance under treatment in the continuous mode [3].

The goal of the present work was to study the application of a continuous centrifugal planetary mill for the activation of the salt mixture to obtain the solid solution $\text{ZrO}_2\text{-8 mol. \% Y}_2\text{O}_3$ after its subsequent heating and to investigate the possibility to use nanopowder obtained at low temperature for sintering dense high-quality ceramics.

EXPERIMENTAL

A longitudinal section of the centrifugal mill of continuous action is shown schematically in Fig. 1. The case (1) of the mill is composed of coaxial cylinders with shaft (2) at their axis. Shaft (2) carries sections fixed on it; the sections contain upper and lower pressure plates (3) and (4), as well as the shafts for ring-shaped milling bodies that are fixed on pressure plates at equal distances from the central shaft. Milling bodies shaped as round discs with orifices in the centre and milling bodies with the orifices displaced from the centre are on the shafts. The size of orifices in discs is much (2–3 times) larger than the shaft diameter. Milling bodies (discs) are united in packs separated by baffles. In these packs, milling bodies with central orifices alternate with milling bodies having the orifices displaced from the centre. Pressure plates have holes for the central shaft and grooves for rigid connection with the shaft which has an out-dent. The sections are detachable, which provides the possibility to replace milling bodies after dismantlement. The housing with fittings for loading the initial material and discharging the treated material is in the case with the possibility to supply the liquid in order to cool the housing.

The mill operates in the following manner. The material to be ground enters the internal

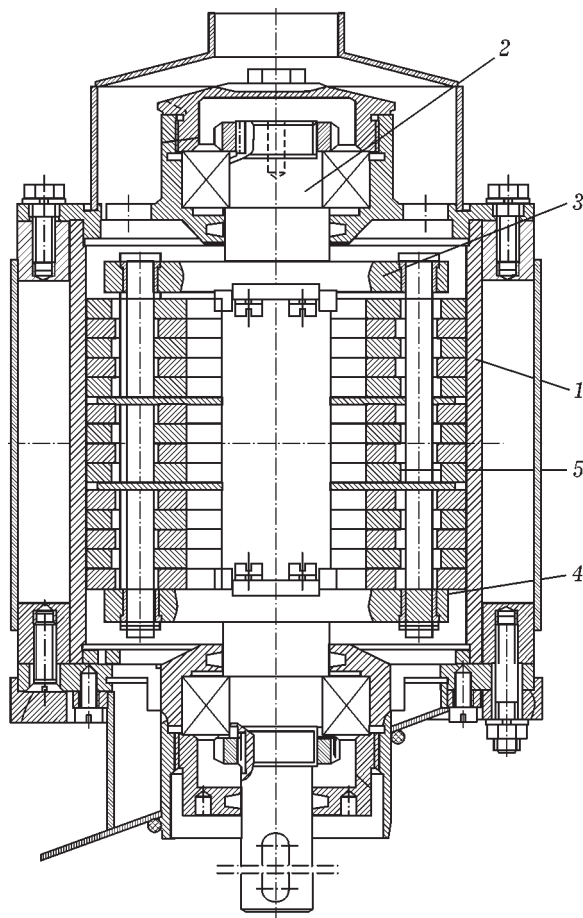


Fig. 1. Centrifugal disc mill of continuous type: 1 – inner cylinder; 2 – main shaft; 3, 4 – pressure plates; 5 – disc-shaped milling bodies.

cylinder of the mill through the fitting in the upper part. Shaft (2) induces rotation of sections and packs with milling bodies on shafts. Getting on the upper pressure plate of each section, the material moves under the action of centrifugal forces to the wall of the internal cylinder and is affected by the action of milling bodies that either roll (milling bodies with orifices in the centre) or strike (milling bodies with orifices displaced from the centre) at the wall. During the rotation of the central shaft, the discs with central orifices interact with the shafts only during speeding up. Quite contrary, discs with displaced orifices interact with the shafts all the time thus providing shock and pulling of the disc along the case wall. Adjustment of the rotation frequency of the main shaft allows one to vary the productivity of the apparatus. At present, mills allowing one to treat up to 35 kg of the material per hour

have been manufactured. In the present work, the joint treatment of a mixture of zirconium oxynitrate and yttrium carbonate was carried out using the laboratory version of centrifugal mill with the productivity of 600 g/h. To prevent possible contamination of the material with the wear material, the discs and the inner cylinder of the laboratory mill were made of metal zirconium.

After passing the salt mixture corresponding to the composition 92 % ZrO₂ and 8 % Y₂O₃ through the mill, powders were subjected to thermal treatment for 3 h at a temperature of 600, 800 and 1000 °C. The X-ray phase analysis of the powders and materials sintered from them was carried out using an X-ray diffractometers DRON-4 (CuK_α radiation, graphite monochromator) and a Bruker D8 Advance. Determination of crystallite size in powders was carried out with the help of PowderCell 2.4 programme with compulsory input of the parameters of standard samples recorded under identical conditions.

Specific surface of the powders was determined using the Katakon sorption meter by means of the thermal desorption of nitrogen, and the micrographs of sintered ceramics were taken with the help of Hitachi TM-1000 microscope.

Disaggregation of the synthesized powders was carried out using the laboratory planetary mill AGO-2M; the cylinders and balls were made of wear-resistant ceramics based on ZrO₂. Disaggregation was carried out at the acceleration of 10g for 15 min using the ceramic balls 5 mm in diameter, in acetone. The curve of size distribution was obtained with the Nicomp 380 DLS particle analyser in a weakly acidic (pH 3.5) aqueous suspension. Powders were pressed through single-axial dry pressing into cylindrical tablets 6.5 and 10 mm in diameter and 2.5–3 mm high under the pressure of 2 t/cm². Tablet sintering was carried out in a VP04/17 furnace at the heating rate of 300 °C/h and exposure for 1.5 h or in dilatometers DL-1 and Netsch DIL203C. The raw density was determined using the geometric method; the density of sintered tablets was measured using hydrostatic weighing.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of products obtained after mechanical activation and thermal treatment of the salt mixture are shown in Fig. 2.

The most intense peak in Fig. 2, a ($2\theta = 10$ degree) corresponds to a 100 % peak of ZrO(NO₃) · 2H₂O. The X-ray diffraction patterns of the mixture after mechanical treatment is a set of reflections related to the initial reagents and intermediate products of their interaction (see Fig. 2, a). After thermal annealing at 600 °C the only identifiable product becomes the cubic modification of zirconium oxide (see Fig. 2, b) with crystallite size 15–17 nm (Table 1) and lattice parameter equal to 5.135 Å. The data of X-ray phase analysis do not allow us to assess the completeness of reaction (2) under the accepted conditions because even in the absence of stabilizing cations thermodynamically equilibrium modifications of zirconium oxide with this crystallite size are tetragonal or cubic [4, 5]. Annealing of the product of mechanical activation at higher temperatures results in the appearance of the reflections of monoclinic modification, along with an increase in crystallite size at 1000 °C (see Fig. 2, c) and retrieval to the monophase solid solution at 1300 °C.

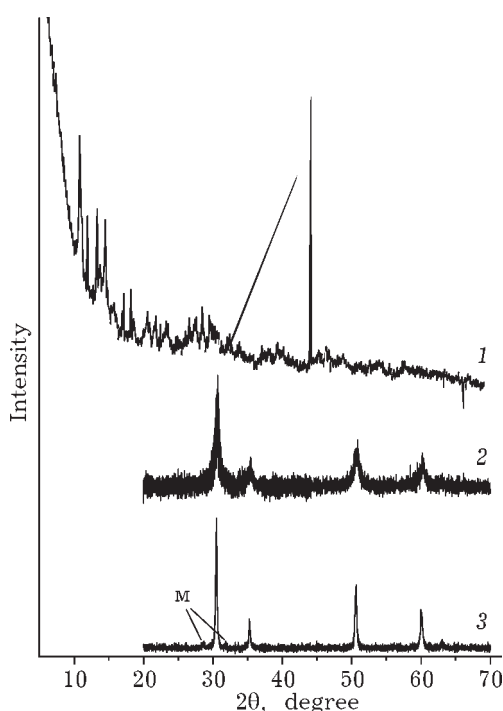


Fig. 2. X-ray diffraction patterns of the salt mixture: 1 – after single passing through the flow centrifugal mill; 2, 3 – after thermal treatment of the activated mixture at 600 and 1000 °C, respectively; arrows mark the reflections assigned to the monoclinic modification of ZrO₂.

TABLE 1

Characteristics of thermally treated mechanically activated salt mixture

Annealing temperature, °C	Phase composition	S_{sp} , m ² /g	Crystallite size, nm	Pressing, t/cm ³	Sintering, g/cm ³ at temperature, °C	
					1300	1550
600	100 % cub.	9.6	16.5	2.87	3.49	4.49
800	100 % cub.	6.3	14.5	2.87	3.43	4.20
1000	92 % cub.-8 % mon.	2.6	75	2.94	3.44	4.24
1300	100 % cub.	—	80	—	—	5.4
600 + disaggregation	100 % cub.	—	—	—	—	5.91

Note. Blank means the absence of data.

So, mechanical and subsequent thermal treatment of the mixture of reagents up to 1000 °C involves insertion of yttrium cations into the lattice of zirconium dioxide, however, the extent of this process does not reach 100 %. A part of ZrO₂ grains do not have yttrium ions in the amount sufficient for stabilization of the cubic modification. In the case if a growing grain exceeds in size the critical value, it is transformed into the monoclinic modification. At higher temperatures, increased efficiency of diffusion mass transfer brings the process of insertion of the stabilizing cations to the completeness. The transition into the monoclinic modification is accompanied by a substantial increase in the volume of zirconium dioxide, which causes distortions of particle packing in the pressed sample, which is clearly pronounced on the dilatometric sintering curve (Fig. 3, a). Nanocrystalline powder (~15 nm) of which the pressed sample is composed exhibits high activity to sintering. Intense shrinkage of the sample starts at the temperature which is extremally low for zirconium oxide, 820 °C. However, later on, due to the transition of the grains into the monoclinic phase, the sample gets swollen. Sintering resumes only after the transition of all the powder particles into the cubic phase.

Evidently, distortion of particle packing during sintering has a negative effect on the final density of agglomerated samples, which does not exceed 75 % of theoretically possible value even at 1550 °C (see Table 1).

Another unfavourable factor for obtaining high density is aggregation of nanopowder, which is caused by thermal annealing at a tem-

perature of 600–800 °C [6, 7]. This is evidenced, for example, by the discrepancy between the data on the average crystallite size obtained from X-ray data and calculated on the basis of the values of specific surface using equation $D = 6/(S\rho)$ where ρ is the density of zirconium oxide; S is its specific surface. Even for annealing temperature of 600 °C, the size of particles (in our case dense aggregates) turns out to be 6.5 times smaller that particle size obtained from X-ray data.

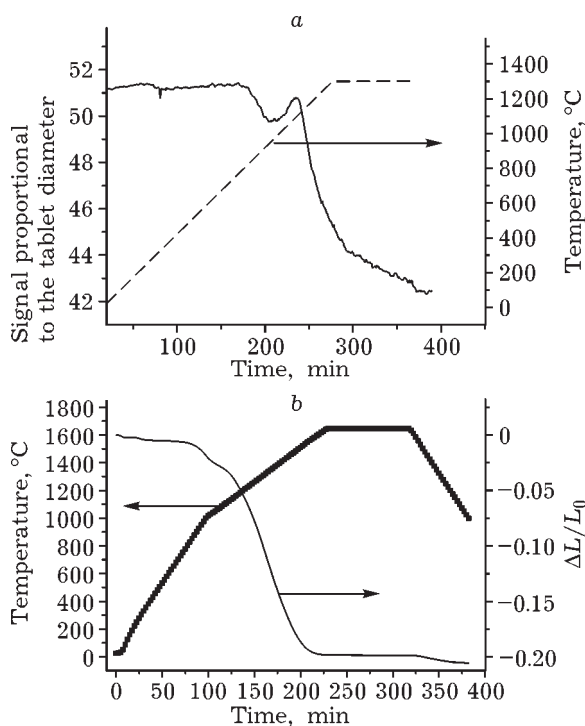


Fig. 3. Dilatogram of sintering the tablet pressed from mechanically activated mixture annealed at 800 °C (a), pressed from the mixture annealed at 600 °C and disaggregated (b). L_0 is the initial height of the sample.

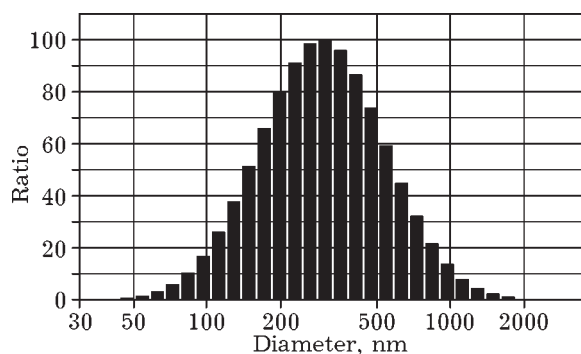


Fig. 4. Size distribution of the particles in disaggregated powder.

To destroy the largest aggregates that create substantial non-uniformities in density distribution over the pressed sample and are responsible for the formation of macro defects during sintering, disaggregation of powder annealed at 600 °C was carried out in the soft mode. The curve of size distribution (Fig. 4) unambiguously points to the presence of only submicrometer particles in disaggregated powder. As a result, the dilatometric curve of sintering the sample pressed from this powder (see Fig. 3, b) drastically changes its appearance. Intense shrinkage starts at the same temperature but the region of sample expansion is absent. The destruction of aggregates is likely to cause further homogenisation of the powder. The size of regions with high and low yttrium content does not exceed the size of crystallites uniformly spread over the volume. During heating the pressed sample, levelling of the concentrations of stabilizing cation between nanocrystallites occurs even before the start of grain growth, so it becomes possible to avoid the expansion region on the dilatometric curve. As a consequence, the density of sintered material turns out to be much higher and reaches 90 % of the theoretical value even at 1300 °C, 97 % at 1450 °C and >99 % at 1600 °C. The microstructure of a dense sample composed of the grains 10–20 μm in size is presented in Fig. 5. It demonstrates almost total absence of pores.

According to EDS, well faceted black crystals distributed over the whole surface of the image are composed of aluminium oxide; the nature of their formation remains unclear yet. The crystals are observed over the whole sam-

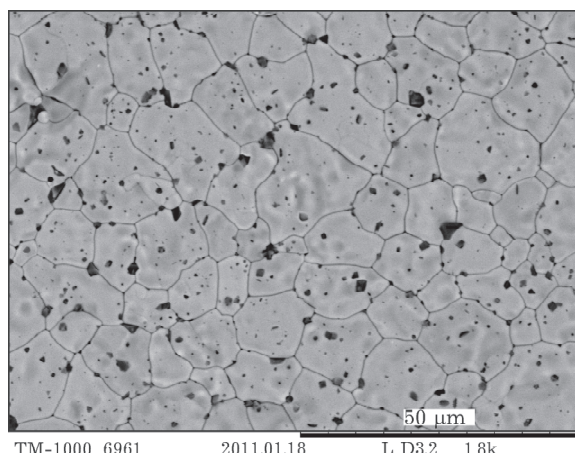


Fig. 5. Microstructure of sample sintered at 1600 °C. Density: 5.91 g/cm³.

ple depth; they are likely formed due to the dissolution of aluminium from the ceramic substrate of the dilatometer at sintering temperature >1500 °C [8, 9]; later on, during cooling it gets segregated mainly at grain boundaries [10].

Some characteristics of the mechanically activated powder mixture after annealing at different temperatures and the densities of tablets sintered from the mixture are presented in Table 1.

CONCLUSION

Low-temperature synthesis of nanopowder having the composition ZrO₂–8 mol. % Y₂O₃ was performed using mechanical activation of the mixtures of hydrated salts of zirconium and yttrium in a flow centrifugal mill of continuous type. The powder is easily moldable by means of dry pressing and is sintered in the air; the density of the powder after that exceeds 99 % of the theoretical density of zirconium dioxide. The high productivity of the mill opens the possibility of practical implementation of this method on the industrial scale.

REFERENCES

- 1 Strelov K. K., *Teoreticheskiye Osnovy Tekhnologii Ogneupornykh Materialov*, Metallurgiya, Moscow, 1985.
- 2 Karakchiev L. G., Avvakumov E. G., Vinokurova O. B., Gusev A. A., Lyakhov N. Z., *Zh. Neorg. Khim.*, 49, 5 (2004) 820.
- 3 RU Pat. No. 44265, 2005.

- 4 Wu N.-L., Wu T.-F., Rusakova I. A., *J. Mater. Res.*, 16 (2001) 666.
- 5 Mayo M. J., Suresh A., Porter W. D., *Rev. Adv. Mater. Sci.*, 5 (2003) 100.
- 6 Rhodes W. H., *J. Am. Ceram. Soc.*, 64 (1981) 19.
- 7 Lange F. F., *J. Am. Ceram. Soc.*, 67 (1984) 83.
- 8 Navarro L. M., Recio P., Jurado J. R., Duran P., *J. Mater. Sci.*, 30 (1995) 1949.
- 9 Feighery A. J., Irvine J. T. S., *Solid State Ionics*, 121 (1999) 209.
- 10 Ross I. M., Reinforth W. M., McComb D. W., Scott A. J., Brydson R., *Scripta Mater.*, 45 (2001) 653.