

Synthesis, morphology, and compactibility of tetragonal zirconia nanopowders

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Fine-grained powders of tetragonal zirconia have been obtained by joint precipitation from aqueous zirconium and yttrium nitrate solutions followed by synthesis under thermal decomposition of hydroxides. The powders show three ordering levels, namely, conglomerates, agglomerates, and "primary" particles. The powder consists mainly of large ellipsoidal conglomerates of 1.5 to 2 μm size, the smaller agglomerates of 0.5 to 1 μm size and mostly irregular shape forming the minor fraction. Both conglomerates and agglomerates consist of rounded or irregular "primary" particles of 30 to 60 nm size. The studied tetragonal zirconia powders show a good compactibility providing the attainable high relative density (48 %) under a reasonable compacting pressure (256 MPa).

Высокодисперсные порошки тетрагонального оксида циркония получены методом совместного осаждения из смеси водных растворов азотнокислых солей циркония и иттрия с последующим синтезом при термическом разложении гидрооксидов. Порошки имеют три уровня организации: конгломераты, агломераты и "первичные частицы". Основная часть порошка представлена большими конгломератами эллипсоидальной формы с размерами 1,5–2 мкм, меньшая часть — агломератами средних размеров 0,5–1 мкм в основном неправильной формы. Конгломераты и агломераты состоят из "первичных частиц" округлой или неправильной формы с размерами 30–60 нм. Исследованные порошки тетрагонального оксида циркония обладают хорошей уплотняемостью, позволяющей достигать высокую относительную плотность (48 %) при приемлемом давлении прессования (256 МПа).

Yttrium stabilized zirconia find use in various industrial fields as transformation-hardened products, catalysts and catalyst supports, fuel cells, thermal barriers, buffering, optical coatings, etc. [1–9]. In countries where atomic power is used widely, the matrix fuels [10], actinoid transmutation targets [11], matrices for radioactive waste insulation [12] based on zirconia are searched for. The efforts of researchers are directed to preparation of non-agglomerated, highly dispersed, relatively inexpensive powders with the particles of required phase composition, homogeneous in size and

shape. A great attention is given to so-called "soft" powders prepared by "wet" techniques (precipitation from solutions, hydrolysis, hydrothermal synthesis, sol-gel method, etc.). According to [2–6], such powders show the coherent scattering regions (CSR) size from 2 to 27 nm, "primary" particles from 10 to 70 nm, agglomerates and conglomerates from 180 nm to 10 μm . The powders prepared by hydrothermal and solvothermal techniques exhibit best morphologic characteristics, however, those are relatively expensive and difficult in realization. The joint precipitation tech-

nique of poorly soluble compounds combines a sufficiently high quality of the powders being prepared and reasonable realization costs. The purposes of this work were to study the morphology and compactibility of tetragonal zirconia powders synthesized during thermal decomposition of zirconium and yttrium hydroxides prepared by joint precipitation from a corresponding mixture of nitrate solutions.

The tetragonal zirconia was synthesized during thermal decomposition of zirconium and yttrium hydroxides prepared by joint precipitation from a mixture of aqueous solutions. Yttrium nitrate of their salts was obtained by nitric acid treatment of yttrium oxide Y_2O_3 and zirconium nitrate, by the similar treatment of zirconium hydroxide prepared by hydrolysis of zirconium sulfate $Zr(SO_4)_2 \cdot 2H_2O$. The zirconium and yttrium nitrate solutions were mixed together and the precipitation was carried out using 25 % ammonium hydroxide solution. The precipitate was dried for 20 to 25 h at 30–40°C and then ground in a ball mill at the powder/milling balls weight ratio of 1/10. The hydroxide precipitate was heat treated at 500 and 600°C for 0.5 to 0.75 h. The zirconium and yttrium nitrates were used in a ration providing the obtaining of zirconia comprising 5.5 wt. % yttria after the precipitate heat decomposition.

To study the processes occurring during the precipitate heat treatment, the thermogravimetric/differential thermal analysis (TG/DTA) was applied using a Q-1500D derivatograph in the temperature interval 20 to 1000°C at the heating rate of 12°C/min. The phase composition of the heat-treated precipitate was determined by X-ray phase analysis (XPA) using a DRON-1.5 diffractometer (Cu K_α) and the average size of the CSR was calculated from the half-height width (β) of the main X-ray line [13]. The specimens were formed from the powder by axial compaction. The sample apparent density was measured by hydrostatic weighing. The tetragonal zirconia powder morphology was studied using a Tesla-BC-613 transmission electron microscope (100 kV accelerating voltage). The powders dispersed in water were captured by an acetyl cellulose film that was used as a substrate. The local powder state (crystalline or amorphous) was examined by micro-diffraction method.

The dried precipitate consisted of soft porous formations of 15 to 30 mm size. After the grinding, there was a fine white

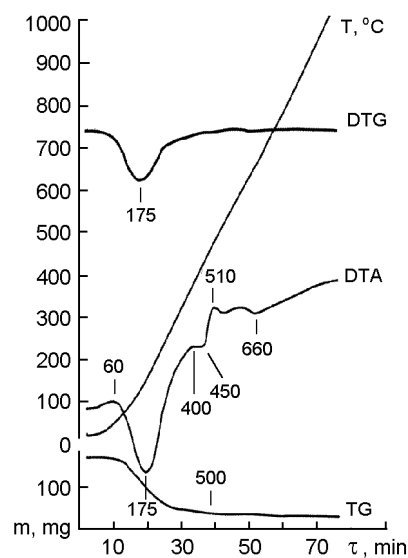


Fig. 1. TG/DTA results for a powdered mixture of zirconium and yttrium hydroxides.

powder. The TG/DTA data on the powder material are presented in Fig. 1. The DTA curve shows two extremes corresponding to one endothermic and one exothermic process. An intense endothermic peak appears within the 60 to 400°C temperature range with a minimum at 175°C. The maximum weight loss corresponding to the steeply dropping section of the TG curve (Fig. 1) is observed in the 100–300°C interval and corresponds to the endothermic DTA peak. An inflection point is in the TG curve at 175°C corresponding to the DTG curve extreme. The weight loss decreases considerably in the mildly sloping section of the TG curve within the 300–450°C interval and is substantially over in the 450–1000°C range. The exothermic effect in the DTA curve within the 450–660°C interval peaked at 510°C is characterized by a substantially constant sample weight (Fig. 1, TG curve). No effects are observed in the DTA curve above 660°C and in TG and DTG ones above 450°C.

The XPA examination of the dry precipitate heat-treated at 500°C for 0.75 h shows halos typical of amorphous state forming a background for several widened X-ray lines. The first high-intensity halo having an appreciable maximum at 31–32° lies within the 22–37° angular range. The second halo arranged within the 42–64° interval has a low intensity and a weak maximum at 52–53°. The halos have been established before to correspond to amorphous zirconia formed due to thermal decomposition of zirconium

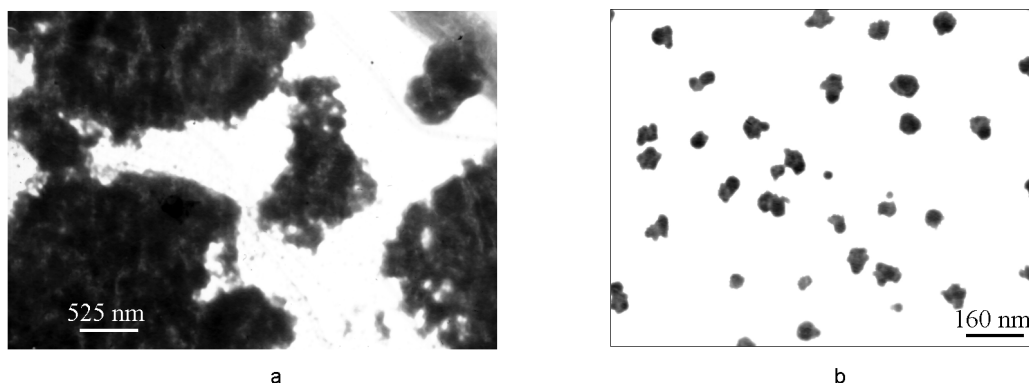


Fig. 2. Transmission electron microscopy of tetragonal zirconia powder: conglomerates and agglomerates (a) and "primary particles" (b).

hydroxide [14] and carbonate [15]. The X-ray lines seen against the halo background correspond to tetragonal zirconia. The diffraction pattern of dry precipitate heat treated at 600°C for 0.5 h shows no halos and the tetragonal zirconia lines observed in the above-mentioned case show an increased intensity. The CSR size is 28 ± 3 nm.

Thus, the precipitate heat treatment in the 60 to 400°C range causes the hydroxide decomposition and amorphous zirconia formation. The crystallization of tetragonal zirconia starts at 500°C and is completed at 600°C.

The morphology of the tetragonal zirconia powder so obtained was examined using transmission electron microscopy (TEM). The material is a powder consisting mainly of large ellipsoidal conglomerates of 1.5 to 2 μm size (Fig. 2a). The minor fraction is presented by medium size (0.5 to 1 μm) agglomerates of predominantly irregular shape. Both conglomerates and agglomerates consist of "primary particles" of 30 to 60 nm size (Fig. 2b). The "primary particles" show a rounded or irregular shape and consist of one or more crystals. Thus, the CSR size is close to that of the smallest "primary particles". The synthesized material is thus a finely dispersed powder characterized by at least three ordering levels (conglomerates, agglomerates, and "primary particles").

The compactibility is among the important characteristics of powders defining the practical use thereof. In Fig. 3, the dependence of relative density on the uniaxial cold compaction pressure for tetragonal zirconia powders is presented. As the compaction pressure increases from 64 to 256 MPa, the relative density goes up from 42 to 48 %.

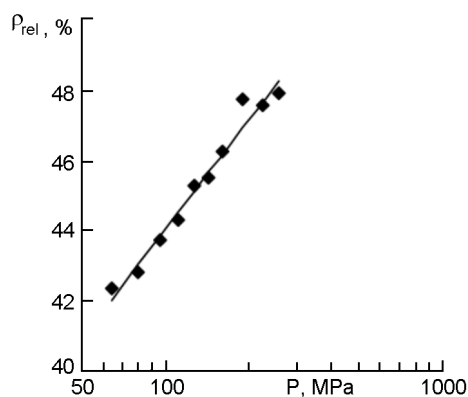


Fig. 3. Relative density of samples prepared from tetragonal zirconia powder as a function of uniaxial cold compaction pressure.

The dependence is described well enough by the equation [8]

$$\rho_{rel} = m \ln P + \rho_0,$$

where ρ_{rel} is the relative density, per cent; P , the uniaxial cold compaction pressure, MPa; m and ρ_0 , constants. Similarly to [8, 9], it has been found that as the compaction pressure increases, the specimens volume decrease due to partial disruption of the powder conglomerates and likely agglomerates.

In [1], zirconium and yttrium hydroxides were co-precipitated by aqueous ammonia from mixed zirconium oxychloride and yttrium nitrate solutions. Despite of difference in the initial salts, the results obtained are somewhat similar to our ones. According to the TG/DTA data, the position of the endothermic peak corresponding to thermal decomposition of hydroxides is substantially identical with that found by us. The maximum weight loss corresponds to that extreme, too. However, the inflection point in the TG curve is observed at 140°C. The

weight loss continues up to 1000°C. The exothermic effect in the DTA curve corresponding to crystallization lies within 450 to 525°C range and is peaked at 475°C. The TG/DTA results being similar, the powder phase composition differs considerably. After the heat treatment at 600°C, the powder contains 15 to 18 vol. % of monoclinic zirconia along with cubic and tetragonal modifications. In our case, the powder is obtained that contains no monoclinic oxide. The powders obtained in [1] are easy to disruption, similar to our ones, that is, show a "friability effect". The "primary particles" are 20 to 60 nm in diameter, that is close to our results.

The tetragonal zirconia powders obtained by joint precipitation in [2] had the CSR size of 22 to 27 nm that substantially coincides with our results within the measurement accuracy. Some authors report smaller CSR sizes amounting 8 to 13 nm [3–5] and 2 to 4 nm [6] for tetragonal zirconia powders prepared by hydrothermal and solvothermal methods, i.e., using more expensive and complicated techniques. The "primary particles" of powders obtained both by joint precipitation [1, 2] and by hydrothermal technique [5] are of 20 to 70 nm size. The "primary particles" of tetragonal zirconia prepared in this work fall in that range. The more complicated hydrothermal technique provides the "primary particles" having the size at the level of 10 to 15 nm [4]. The zirconia powder preparation parameters effect decisively the conglomerate and agglomerate size. In the powders obtained by joint precipitation, the size is of 200 nm [1] to 10 µm [2] while in those prepared by hydrothermal technique, up to 180 nm [5]. As mentioned above, the powders studied in this work show the conglomerate size of 1.5 to 2 µm and the agglomerate one of 0.5 to 1 µm, that is comparable with data from [1].

In [7], samples of zirconia with the relative density 43 % of the theoretical one were prepared from tetragonal zirconia powders obtained hydrothermal technique using the slip casting. The relative density was increased up to 48.8 % after cold isostatic compaction at 400 MPa. The specimens formed by uniaxial compaction at 256 MPa from the powders obtained in this work by joint precipitation show the relative density 48 %. Thus, those powders are more "soft" than those obtained in [7], since the same relative density can be obtained under the uniaxial compaction at al-

most halved pressure. In [8], the specimens having the relative density 48 % were obtained from two kinds of jointly precipitated powders only under 350 and 400 MPa pressure. In [9], the specimens compacted from two jointly precipitated zirconia powders at 200 MPa had the relative density only 45 % and 39 %.

In spite of similar morphology (conglomerate, agglomerate, and "primary particle" size and shape), the powder prepared using the method described in this work has an best compactibility and exceeds some analogs from abroad in that sense. This seems to be due to a lower strength of conglomerates and agglomerates as compared to the powders obtained in [7–9]. In contrast to the powders prepared in [7], our powder contains no other phases in addition to tetragonal one.

To conclude, single-phase tetragonal zirconia powders have been prepared by joint precipitation from a mixture of zirconium and yttrium nitrate aqueous solutions followed by thermal decomposition of hydroxides at 600°C for 1 h. According to electron microscopy data, the powders consist mainly of large ellipsoidal conglomerates of 1.5 to 2 µm size, the minor fraction being presented by medium size (0.5 to 1 µm) agglomerates of predominantly irregular shape. Both conglomerates and agglomerates consist of "primary particles" of 30 to 60 nm size. That is, the finely dispersed powder is characterized by at least three ordering levels (conglomerates, agglomerates, and "primary particles"). The coherent scattering region size is 28±3 nm, as determined using the main X-ray line widening. The powders show an best compactibility as compared to some analogs from abroad, thus providing a high relative density (48 % of theoretical one) at lower compaction pressures (256 MPa) and technological advantages in production of ceramic produce.

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Синтез, морфологія й ущільненість нанопорошків тетрагонального оксиду цирконію

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Високодисперсні порошки тетрагонального оксиду цирконію отримано методом сумісного осадження із суміші водних розчинів азотнокислих солей цирконію та ітрію з наступним синтезом при термічному розкладанні гідрооксидів. Порошки мають три рівні організації: конгломерати, агломерати та "первинні частки". Основна частина порошку представлена великими конгломератами еліпсоїдальної форми з розмірами 1,5–2 мкм, менша частина — агломератами середніх розмірів 0,5–1 мкм в основному неправильної форми. Конгломерати й агломерати складаються з "первинних часток" округлої або неправильної форми з розмірами 30–60 нм. Досліджені порошки тетрагонального оксиду цирконію мають добру ущільненість, яка дозволяє досягати високу відносну густину (48 %) при прийнятному тиску пресування (256 МПа).