# Synthesis of $Al_2O_3$-$ZrO_2$ Powders from Differently Concentrated Suspensions with a Spray Drying Technique

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**Abstract.** The composite powders of aluminium and zirconium oxides containing 10, 50 and 90 mol % $Al^{3+}$ without a stabilizer have been obtained from suspensions using a spray drying method. The powders obtained at equal mole ratios of zirconium and aluminum in the original solution (0.5:0.5 mol/l) have the largest contents of cubic and tetragonal phases of $ZrO_2$, strictly uniform distribution of phases and the largest value of the specific surface area. The particles with two different morphologies have been obtained: crystalline particles of oxides uniformly distributed in a particle and particles in membrane consisting of zirconium oxide or mixed oxides. It has been experimentally shown that zirconium oxide stabilizes the amorphous phase of aluminum oxide, and aluminum oxide increases the temperature of crystallization of zirconium oxide.

## INTRODUCTION

$Al_2O_3$–$ZrO_2$ composite ceramics is a promising material since it possesses the crack resistance and hardness higher than pure aluminium oxide and zirconium oxide, respectively [1–3]. The combination of mechanical properties and a proper biocompatibility makes the use of the $Al_2O_3$–$ZrO_2$ composite ceramics rather promising in dentistry and orthopedic surgery (tooth and joint implants) [4]. The $Al_2O_3$–$ZrO_2$ composite ceramics can be produced via mixing the aluminum and zirconium oxide powders. However, the nanoscale composite powders are more preferable to apply for the production of composite ceramics. Aluminum and zirconium oxides are not mutually-soluble, however, in the nanoscale state they form mixed oxides [4]. The change of $Al_2O_3$ and $ZrO_2$ proportion in the system allows producing the powders of various morphology and phase composition [1, 3–5].

Coprecipitation, reversed precipitation, sol-gel synthesis are considered as the best methods for the obtaining of $Al_2O_3$–$ZrO_2$ nanopowders. We previously described the use of Nano Spray Dryer B-90 for the production of $Al_2O_3$ and $ZrO_2$ nanopowders from strong solutions and suspensions [6,7]. Spray drying is widely used for producing granulated feed materials for compaction process, which is the current industrial method for manufacturing alumina-zirconia femoral heads [8]. The aim of this work is to evaluate the phase composition and morphology $Al_2O_3$–$ZrO_2$ nanopowders prepared from the differently concentrated aluminium and zirconium salts in water suspension by means of spray drying technique.

## METHODS AND MATERIALS

$Al_2O_3$-$ZrO_2$ nanopowder is produced from suspensions prepared from the solutions of aluminum and zirconium salts. Chemically pure zirconium oxynitrate and aluminium nitrate are used in this experiment (INTERCHIM,

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Russia). The salt solutions are prepared with concentration 1 mol/l in distilled water. Then the solutions are mixed in different ratio. The solution concentrations varied from 0.1 to 0.9 mol/l, the $Al^{3+}$ / $ZrO^{2+}$ ratio is 1:9, 1:1, and 9:1. The suspensions are obtained using the method of reversed precipitation in 25% ammonia solution by stirring. Ammonia concentration is more than 20 % in comparison with design value for full deposition of aluminium and zirconium. Separated sediment is repeatedly washed with distilled water, whereupon it was diluted to the concentration 20 %.

The powders are synthesized from suspensions by two methods, namely: filtration and spray drying using the Nano-Spray Dryer B-90 having 140 l/min gas flow rate; 65 % relative spray intensity; T = 70 °C, P = 120 Pa. Powders obtained by filtration are used for the comparison with $Al_2O_3$–$ZrO_2$ samples produced by spray drying technic. Consequently, there are six samples with different $Al^{3+}/ZrO^{2+}$ ratio: three samples are produced by Nano-Spray Dryer B-90 and three ones are synthesized by filtration. The obtained powders are annealed in the atmospheric heater at 1200 ºC during 1 hour.

The specific surface area (SSA) of the powders is characterized using a Brunauer-Emmett-Teller (BET) analyzer Meta Sorbi-M (Russia).

The phase composition of the powders is examined on a XRD-7000 X-ray Diffractometer (Shimadzu). Measurements are conducted using copper radiation (0.03° scanning step). The Rietveld method is applied for the calculation of coherent scattering regions (RCS) of crystallites by means of Powder Cell Program.

The differential scanning calorimetry (DSC) and thermal gravitational analysis (TG) are simultaneously carried out with a Netzsch STA 409 PC analyzer (Germany), with a heating rate of 5 K/min for the powders which are stored during 2 hours at 120 °C.

The microstructure of powders and energy-dispersive X-ray spectroscopy are examined by a scanning electron microscopy (SEM) with a microscope JEOL JSM 7500S (Japan).

## RESULTS AND DISCUSSION

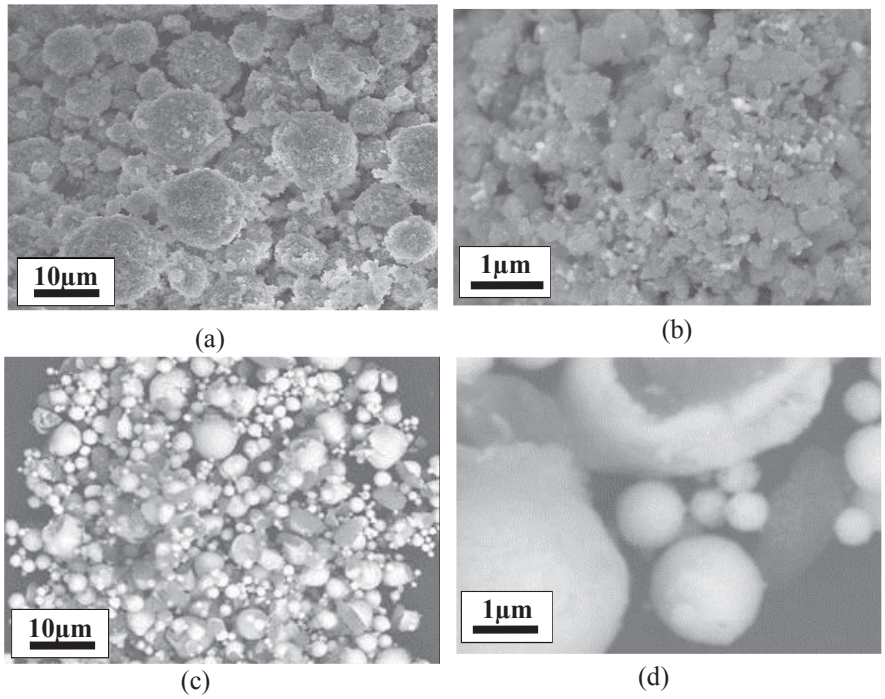


**FIGURE 1.** SEM images of the powders obtained by the spray drying technique: ratio $[Al^{3+}]:[ZrO^{2+}]$ = 0.5:0.5 (*a, b*); 0.1:0.9 (*c, d*) mol/l

According to the paper [9], a phase diagrams of $Al_2O_3$-$ZrO_2$ system show that the highest solid solubility of $Al_2O_3$ in $ZrO_2$ is achieved at $Al_2O_3$ concentration about 7 mol %. However, there are several papers where $ZrO_2$-$Al_2O_3$ powders synthesize with up to 50 mol % of $Al_2O_3$ [4, 10], since $Al_2O_3$ solubility depends on the synthesis

method and condition. Therefore we use borderline concentrations of aluminium and zirconium: from 10 up to 90 mol % of $Al_2O_3$ in the suspension.

SEM-images (Fig. 1) show that the Nano Spray drying technics allow receiving almost spherical particles which seem to be highly prospective for a ceramic articles manufacturing. The particle sizes are from 1 to 11 μm at equal mole ratios of zirconium and aluminum in the original solution and from 0,5 to 0,5 μm for the particles obtained from the suspension comprising 0,9mol/l zirconium salts and 0.1 mol/l aluminum salts.

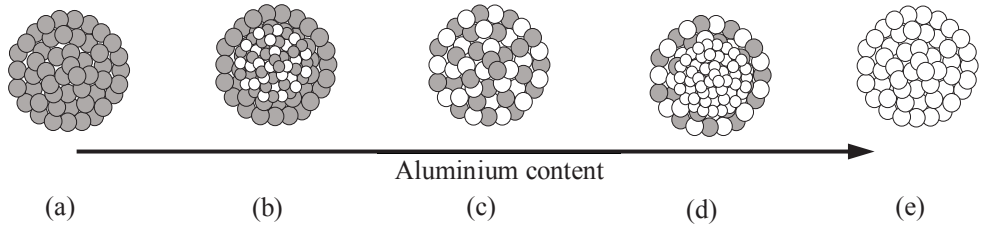


**FIGURE 2.** Phase distribution of $Al_2O_3$–$ZrO_2$ particles depending on the aluminium content:
– $ZrO_2$ – $Al_2O_3$

It is to be said that there are basic requirements for composite nanopowders: a uniformly phase distribution in a system, an absence of hard agglomerates and even phase composition. We analysed two types of powders, produced under different experimental conditions. The SEM analysis of the particles synthesizing from the suspensions at equal mole ratios of zirconium and aluminum has revealed that particles includes $Al_2O_3$ and $ZrO_2$ crystallites uniformly distributed in the system (Fig.1, a, b). According to the energy-dispersive X-ray spectroscopy, the dark particles (Fig.1a and 1b) consisting of zirconium, aluminum and oxygen can be represented by the mixed oxides phase of $Zr(1-x)Al_xO(2-x/2)$ [4]; white particles are zirconium and oxygen. Indeed, the white particles have a greater density as compared with the density of dark one. The second type powder type is the mixture of either oxides in the zirconium oxide membrane (Fig. 1, c, d) or the particles of aluminum oxide in the mixed oxides membrane. Based on these results, we suggest the models of the particle morphology depending upon the ratio between the aluminium and zirconium oxides in the mixture (Fig. 2). This scheme is chosen based on the assumption that if the particles are synthesized at the excessive amount of some oxide ($Al_2O_3$ and $ZrO_2$) then a membrane consist from substance with a greater density. In this case, the particles synthesized at the excessive amount of $Al_2O_3$ have $Al_2O_3$–$ZrO_2$ –membranes; the others synthesized at the excessive amount of zirconium oxide have $ZrO_2$–membranes.

The results of the X-ray analysis of the powders after 1200 °C annealing and the values of specific surface areas are presented in the table 1.

**TABLE 1.** Phase composition and specific surface area of samples

| $[ZrO^{2+}]$ | $[Al^{3+}]$ | Spray dryer | | | Filtration | | |
|---|---|---|---|---|---|---|---|
| | | **Phase composition** | **RCS, nm** | **SSA, $m^2/g$** | **Phase composition** | **RCS, nm** | **SSA, $m^2/g$** |
| 0.9 | 0.1 | c-$ZrO_2$–61.2%<br>t-$ZrO_2$–38.8% | 17.08<br>16.13 | 3.81 ± 0.04 | m-$ZrO_2$–88.8%<br>t-$ZrO_2$–5.8%<br>α-$Al_2O_3$-5.4% | 29.64<br>13.99<br>14.29 | 2.91 ± 0.04 |
| 0.5 | 0.5 | c-$ZrO_2$–12.6%<br>t-$ZrO_2$–54.1%<br>α-$Al_2O_3$-33.3% | 44.02<br>43.08<br>44.02 | 26.54 ± 0.09 | m-$ZrO_2$–32.7%<br>t-$ZrO_2$–51.5%<br>α-$Al_2O_3$-15.8 | 14.77<br>37.22<br>16.19 | 18.81 ± 0.09 |
| 0.1 | 0.9 | m-$ZrO_2$–83.7%<br>t-$ZrO_2$–4.9%<br>θ-$Al_2O_3$–11.4% | 27.78<br>14.57<br>11.93 | 4.98 ± 0.02 | m-$ZrO_2$–76.1%<br>t-$ZrO_2$–6.9%<br>α-$Al_2O_3$–17.0% | 33.87<br>14.77<br>16.64 | 0.70 ± 0.01 |

According to BET-analysis, the powder obtained by the nanospray drying method have the largest value of the specific surface area in comparison with the powders obtained by the filtration method. That is due to the morphology of samples: nano spray drying technique allows synthesizing the spherical particles, which do not undergo to an additional aggregation during the heating. Herewith, the values of coherent scattering regions evident that the crystalline grain sizes of particles extracted by both methods are commensurable with each other. The oxide

particles have the largest value of the specific surface area at the equal oxide ratio in the suspension. These oxide particles do not contain the membrane of a denser phase (Fig. 1, c) which prevents the penetration of gas molecules inside the particles and its adsorption on the particle surface when detecting the specific surface area of the powder.

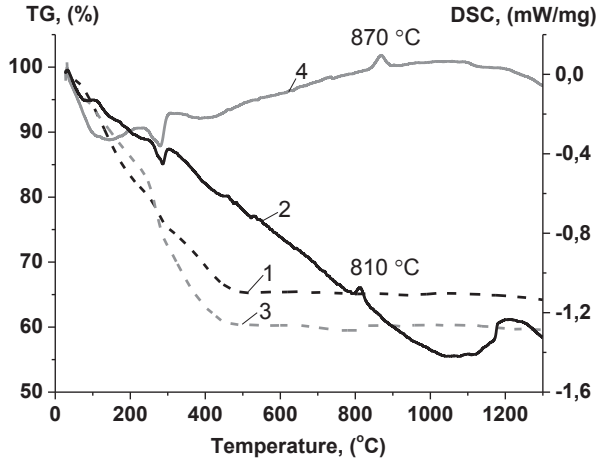


**FIGURE 3.**TG (*1, 3*) and DSC (*2, 4*) curves of powders obtained from suspensions ($[Al^{3+}]$:$[ZrO^{2+}]$ = 0.5:0.5 mol/l) using spray drying (*3, 4*) and filtration (*1, 2*).

According to the results of the X-ray analysis of the powders after 1200 °C annealing (Table 1), the majority of samples contains the lower amount of aluminum oxide crystalline phases than in the original state, or does not contain it at all. This is because the crystallization of aluminum and zirconium oxides starts at higher temperatures in those systems containing the both of these substances.

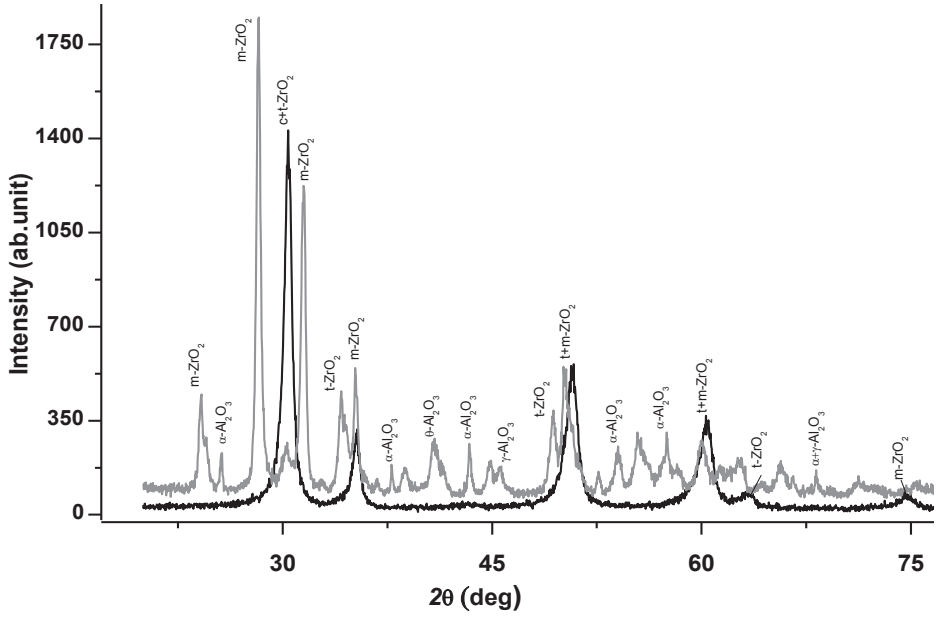


**FIGURE 4.** Diffraction patterns of the powders obtained from suspensions ($[Al^{3+}]$:$[ZrO^{2+}]$ = 0.9:0.1 mol/l) using the spray drying (black curve) and filtration (gray curve) methods after 1200 °C annealing.

According to the data found in the literature [4, 10], the nanocrystal zirconium oxide stabilizes the amorphous phase of aluminum oxide up to 1250 ºC. Actually, the differential scanning calorimetry (DSC) curves presented in the figure 3, show that the exothermic reaction responsible for the crystallization of zirconium oxide is observed at 810 ºC for the powder obtained by the filtration method, and at 870 ºC – for the powder obtained by the spray drying method. There are no other signals corresponding to the formation of a new phase. Thermogravimetric curves show that the samples lose 40 % mass in process of heating at temperatures of 25–400° C and DSK-curves demonstrate the corresponding signals of elimination of crystallization water at 280–290 °C.

The difference in morphology explains the difference in the DSC curves between the powders obtained by the spray drying (Fig. 3, curve 4) and filtration (Fig. 3, curve 2) methods. With the temperature increase, the heat capacity decreases in the samples obtained from suspension by the filtration method, since the annealing decreases the size of particles, and the correlation between them can be destroyed. The particles obtained by the spray drying method originally compose an agglomeration. Hence, the annealing has the lower effect on the heat capacity.

$ZrO_2$ is known to have three polymorphs: monoclinic (m-$ZrO_2$), tetragonal (t-$ZrO_2$), and cubic (c-$ZrO_2$) [10]. The high-temperature cubic and tetragonal phases are more useful for some modern ceramics [11] and can be stabilized at room temperature by incorporating some dopants in the lattice. According to some previous studies [10], tetragonal is the stable crystalline phase, without any stabilizer, at low temperatures in nano and submicron structures of zirconia.

The spray drying method produces a larger amount of cubic and tetragonal phases than filtration. This is with the exception of the particles obtained from the suspension comprising 0.9 mol/l zirconium salts and 0.1 mol/l aluminum salts, i.e. at the excessive amount of zirconium oxide. At the same time, the interpretation of the diffraction patterns is rather complicated. For example, the Figure 4 presents the X-ray analysis of the powders obtained by different methods. According to this figure, the diffraction pattern of the sample obtained by filtration contains the reflections of α-, γ- and θ-$Al_2O_3$ and m, t- and c-$ZrO_2$. Due to this fact, the best accuracy of phase percentage is calculated using the corundum numbersand has the corresponding inaccuracy.

## SUMMARY

The composite powders of aluminum and zirconium oxides have been obtained from suspensions using the nanospray drying method. It has been experimentally shown that the particles with different morphology can be obtained depending on the oxide ratio in the initial suspensions we can synthesize, namely: crystalline particles of oxides uniformly distributed in a particle; particles in membrane consisting of zirconium oxide or mixed oxides. The effect of mutual influence of oxides has been detected for the powders. Thus, zirconium oxide stabilizes the amorphous phase of aluminum oxide; aluminum oxide increases the temperature of crystallization of zirconium oxide and mixed oxides can be formed at a nanoscale level. The powders obtained at equal mole ratios of zirconium and aluminum in the original solution (0.5:0.5 mol/l) by nanospray drying technique have the largest contents of cubic and tetragonal phases of $ZrO_2$, strictly uniform distribution of phases and the largest value of the specific surface area.

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