

# INFLUENCE OF PRECURSOR DISPERSITY AND AGGLOMERATION ON MECHANICAL CHARACTERISTICS OF $92\text{ZrO}_2 - 8\text{Y}_2\text{O}_3$ CERAMICS

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**Abstract.** Ceramics based on the systems of  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  are widely used as constructional materials, catalyst carriers, high-temperature oxygen sensors, materials of fuel cell and so on. In this connection, such properties of these materials as mechanical strength and cracking resistance are of exceptional importance. Phase transitions, producing changes in the chemical composition, crystal structure, and thermodynamic properties of ceramic materials, may be a cause of their destruction. The subject of the present investigation is powder zirconium hydroxide, both pure and Y-stabilized. Phase transformations have been studied well enough in these powders with micron size of particles. However up to now, there have been no systematic attempts to determine an interconnection between powder dispersity and phase transitions (and associated mechanical characteristics). In present work powder precursors of various dispersity were synthesized by sol-gel method allowing to obtain particles with sizes ranging from 40 nm to 5-10  $\mu\text{m}$ . The main purpose of the work was to obtain powders with narrow particle size distribution, that is, essentially monodispersed powders. To characterize the powders obtained, we used the following methods: electron microscopy, laser scattering particle size distribution analysis, and adsorption methods. Experimental results have shown that dispersity of powders under investigation has a profound effect not only on their phase transition temperatures, but also on composition of precursor crystallohydrates. Three points bending measured at 1000 °C for the ceramics fabricated from these precursors also depends on the precursor dispersity.

## 1. INTRODUCTION

Modern high-temperature technology requires new properties of widely used materials. Nano-chemistry makes possible obtaining special properties of well-studied ceramics. For example, in development of ceramics for solid electrolyte in high-temperature oxygen sensors, materials with new chemical, mechanical, and sensoric properties can be ob-

tained on the basis of well-known systems of  $\text{ZrO}_2\text{-Y}_2\text{O}_3$ ,  $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-HfO}_2$ ,  $\text{ZrO}_2\text{-CeO}_2\text{-HfO}_2$ . Sol-gel synthesis of precursors for fabrication of ceramics allows to obtain near the mono-dispersed powders over a wide range of particle sizes. However, as-synthesized powders have a greater tendency to agglomerate. Degree of agglomeration increases with a decrease of particle size. There are many ways to suppress agglomeration:

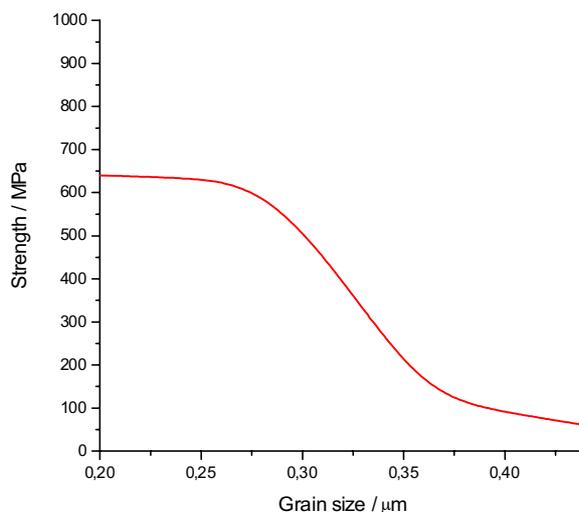
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- Synthesis temperature depression allows controlling strength and extent of agglomeration of powder precursors and also decreases the quantity of crystallisation water in precipitated hydroxide crystallohydrates.
- The use of superficial active substances (SAS), both classic such as ammonium chloride and modern such as dodecylsulphate, TSA in a various measure permits creating a SAS layer (preventing from agglomeration) on the nanoparticle surface. However, this approach is effective in the only case of structural ceramics, but leads to degradation of sensor characteristics of nanoceramics.
- The use of ultrasonic method (USM). Sol-gel synthesis in US (ultrasonic) reactors also permits suppressing agglomeration processes. Moreover, it improves the mixing of the components in reactional mixture. However application of coprecipitation in USM is limited by using the low-energy generator. With high-energy generator, local vaporization of precipitator from reaction mixture at the instant of contact occurs which shifts the stoichiometry of reaction mixture.
- Gel drying. Agglomerates can also be destroyed during gel drying by methods of thermal shock, drying under pressure or drying in a gas jet.
- Precipitation from high-diluted solutions. Low concentrations of the components of reaction mixture and precipitator allow to synthesize low agglomerated powders, but require large volumes of reaction mixture and considerable time periods.
- pH-control and regulation. Acidity of reaction mixture and precipitator defines to a large extent agglomeration processes and represents one of precise instruments of synthesis.

Above mentioned approaches allow to decrease agglomeration, but it is hardly probable that agglomeration processes in nano-dispersed powders will be eliminated.

Moreover, at the present time it is next to impossible to find in reference data on the results of systematic studies of the effect of precursor dispersity on properties of obtained ceramic materials. In [1,2] a dispersity dependence of mechanical characteristics for Y-Zr ceramics at room temperature is given (Fig.1). The general view of this dependence permits to expect improvements of mechanical characteristics of ceramics with a decrease of precursor dispersity.



**Fig. 1.** Grain size dependence of the fracture strength for tetragonal zirconia polycrystals [1].

The present work is a systematic investigation of influence of sol-gel synthesis conditions on particle sizes and agglomeration of precursor powders, and dispersity effect on mechanical and sensoric characteristics of final ceramics.

## 2. EXPERIMENTAL

For investigation we have chosen a composition of 8Y-92Zr whose structure and phase transformations are well-studied. Chemical analysis and XPS surface analysis of final ceramics have shown a good accordance (within 1%) between the composition of the initial reaction mixture and composition of the final ceramics.

A kind of sol-gel method was used, namely back coprecipitation from solutions, was used to synthesize of powder precursors. At that the following parameters were variable: concentrations of reagents and precipitant, pH of reaction medium, reagent adding rate, agitation rate of reaction mixture, and its temperature. Selection of the optimal combination of these parameters allows to obtain powder precursors with particle sizes from 50 nm to 10  $\mu\text{m}$  [3,4].

As starting components, the following salts were used:  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (c.p.g.) and  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (c.p.g.). A 1.25M ammonium aqueous solution was

used as a precipitant. The synthesis was carried out at 5 °C.

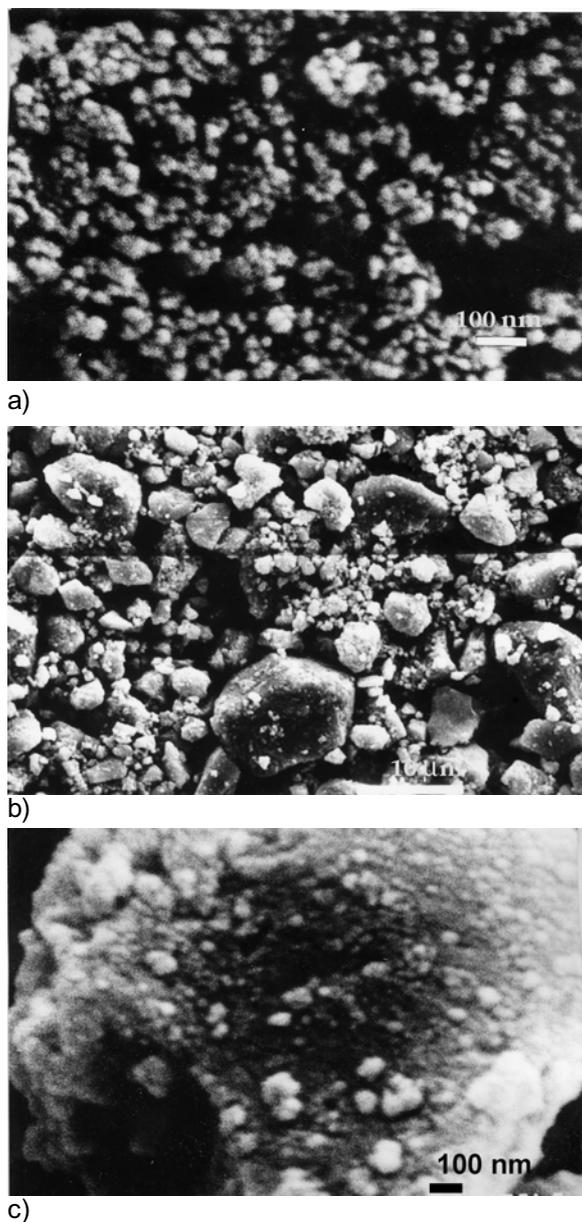
Gel synthesized was washed with distilled water on a Buchner filter until neutral pH of the gel and dried under pressure between polished glass plates at 120 °C. As-obtained powder was calcined at 550 °C. The moulding of ceramic samples was carried out in a steel mould under 45 atm without a binder. Then as-obtained blanks were enclosed in latex shells and treated in a hydrostat under 1500 atm. Ceramic samples formed from this powder were sintered at 1600 °C during 2 hours.

Dispersity of powder precursors after drying and calcination was determined by laser scattering particle size distribution analysis using an HORIBA LA-950. Phase transformation in powder precursors were studied using Shimadzu X-ray diffractometer XRD-6000 and by DSC method with Netsch Pegasus 407. Surface area of the powders was determined by the method of nitrogen adsorption using Technotherm NOVA-1200. Mechanical characteristics of ceramics obtained were defined by three points bending method at 1000 °C.

### 3. RESULTS AND DISCUSSION

An efficient way to control particle sizes of powder precursors is to vary start concentrations of salt solutions added to a precipitant. For the current work, the start concentrations were chosen from 0.01 to 1.2M (see Table 1). Amounts of start components for each of the syntheses were calculated so that 0.1 mole of the  $92\text{ZrO}_2\text{-}8\text{Y}_2\text{O}_3$  composition was obtained. The synthesis presented some difficulties related to a large volume of the reaction mixture of solutions. So, for the solutions of minimum concentrations, the volume of the reaction mixture was about 11 litres.

Fig. 2 demonstrates microphotos of the powder precursors obtained from solutions of different concentrations. In Fig.3 the distribution of particle sizes in the precursors is shown. On the basis of these results the dependence of the mean particle size in precursors on concentrations of salt solutions in reaction mixture was constructed (Fig. 4). It is seen from Fig. 4 that over the range of diluted solutions the mean particle size is slightly changed, but the increase in the concentration up to 0.1 mole/l and more causes a drastic increase in particle sizes of precursors obtained. Most likely, in solutions of such concentrations a great quantity of particle nuclei is formed which begin to integrate and to grow and it results in a sharp rise of particle size.



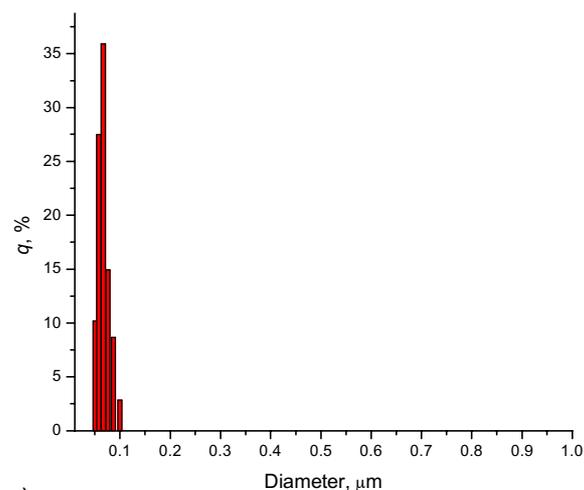
**Fig. 2.** Microphotographies of powder precursors obtained at starting concentrations in reaction mixture: a – 0.01M, b – 1.2M, c - a typical agglomerate forming in 0.05M solutions from particles of 60 nm in size.

Analysis of surface area of the powders was carried out by nitrogen adsorption method, the surface area was determined by BET. The results of the experiments are presented in Table 1.

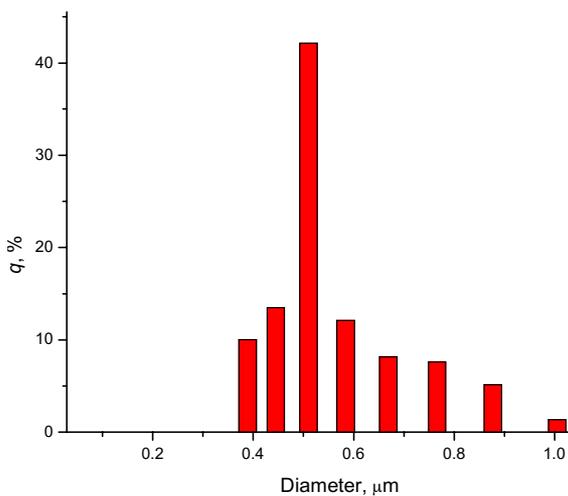
As seen from the table, surface area of the powders increases with the rise of their dispersity. Also it should be noted that a form of obtained adsorption isotherms is strongly dependent on powder pre-

**Table 1.** Characteristics of powder precursors dispersity.

#	Starting concentration M	Mean size nm	Surface area m <sup>2</sup> /g	Temperature of transition to cubic phase, °C
1	0.01	42	140.15	429
2	0.05	58	97.4	444
3	0.1	96	62.1	474
4	0.4	510	14.0	639
5	0.6	815	13.8	675
6	0.8	2400	11.4	685
7	1.2	~10000	-	727



a)



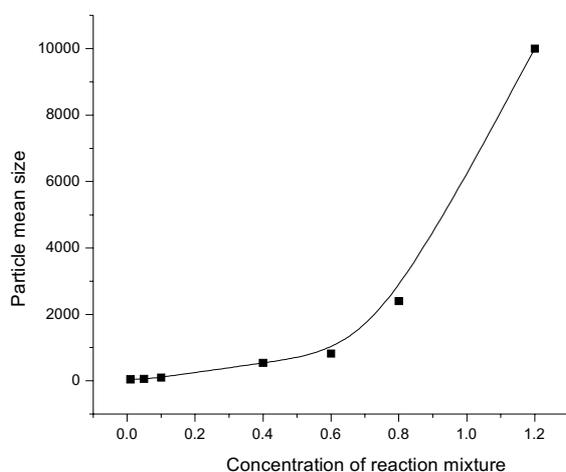
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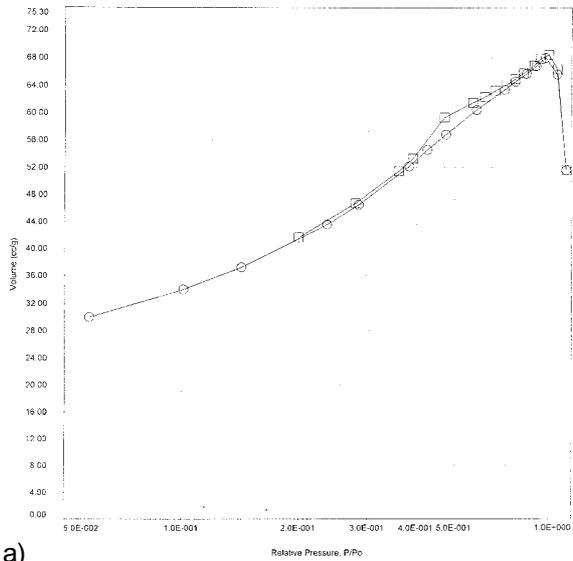
**Fig. 3.** Typical distribution of particle sizes for the sample of #2 – a and #4 – b.

cursors dispersity. Fig. 5 a-c demonstrate the most typical isotherms for the powders obtained. Observed difference between these curves can be explained by formation of two- and three-dimensional agglomerates in precursors at the temperature of liquid nitrogen. Small amounts of such agglomerates are also detected in starting mixtures.

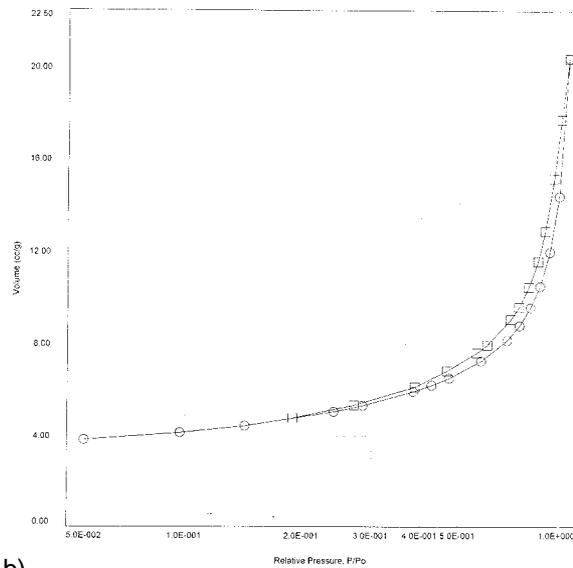
The results of DSC-investigations of powder precursors obtained are presented in Fig. 6. It is evident from the figure that the temperature of a deep exothermic effect observed on heating depends on particle sizes of powder precursor: it changes from 429 to 727 °C for #1 and #7, respectively.

Fig.7 illustrates the results of X-ray diffraction investigations of powder precursors. These data allow to conclude that the effects observed in DSC-

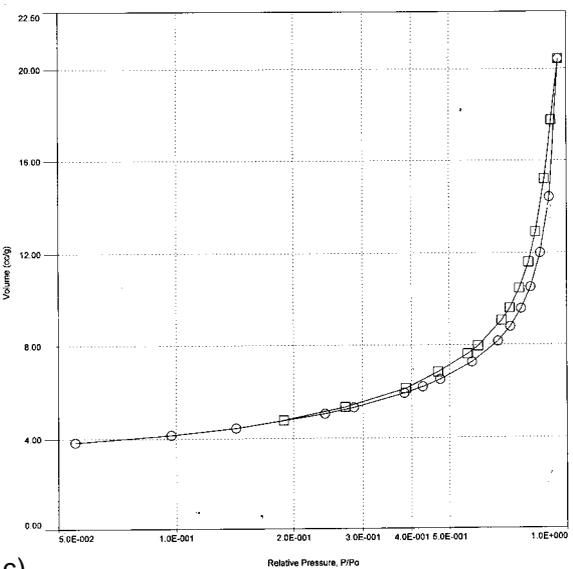
**Fig. 4.** Dependence of mean particle size on concentration of reaction mixture.



a)

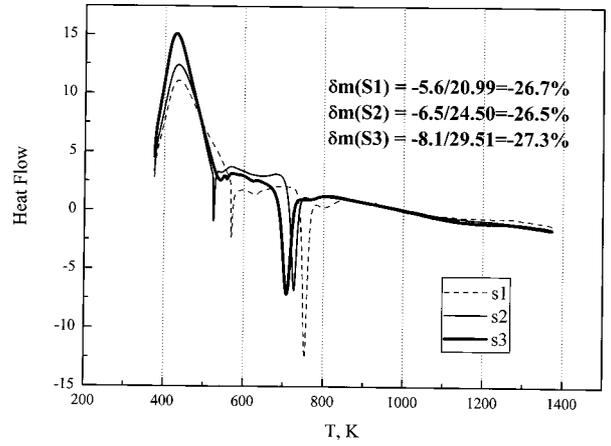


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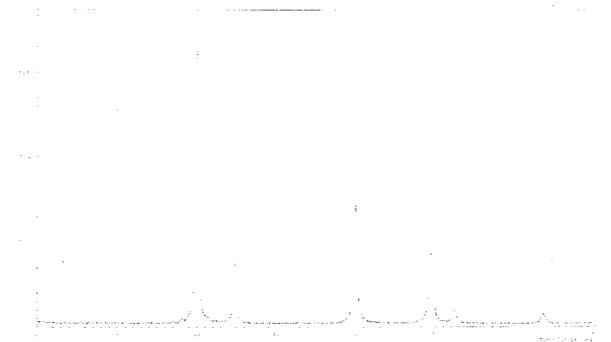


c)

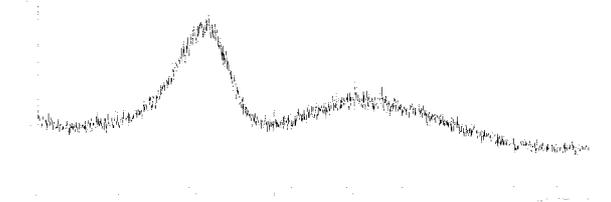
**Fig. 5.** Typical nitrogen adsorption isotherms for powder precursors of different dispersity: a – #1, b – #2, c – #3. ○ – adsorption and □ – desorption curve.



**Fig. 6.** Thermograms of powder precursors 1 – #3, 2 – #2, 3 – #1.



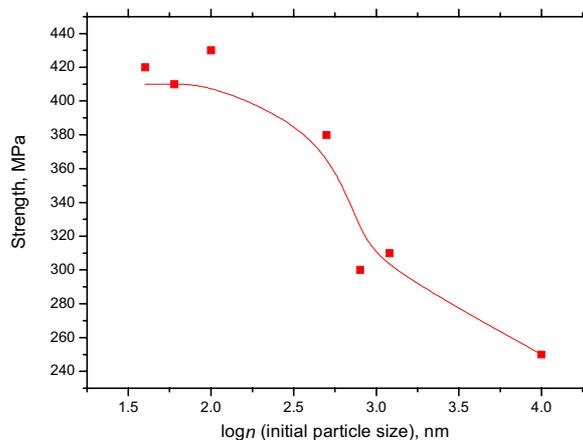
a)



b)

**Fig. 7.** X-ray diffraction patterns for powder #2 before (b) and after (a) calcination.

curves are associated with transitions of powder precursors from amorphous to crystalline state: the start powder has an amorphous structure, the same powder heated at temperature 100 °C more than the temperature of the exoeffect has a cubic structure.



**Fig. 8.** High-temperature mechanical characteristics obtained by three points bending.

Mechanical characteristics obtained by three points bending at 1000 °C are shown in Fig. 8. As can be seen from the figure, mechanical strength of final bulk nano-ceramics increases as dispersity of a powder precursor increases.

## CONCLUSIONS

The main result of the present investigation – dependence of mechanical characteristics of bulk nano-ceramics on powder precursor dispersity – can-

not be thought of as unexpected. Undoubtedly, mechanical characteristics of ceramics must be defined by the size of its grains, but this size depends on precursor dispersity. We plan to continue investigation for other systems in which we hope to obtain sufficiently mono-dispersed powder precursors for bulk nano-ceramics. Observed dependence of forms of adsorption isotherms on powder precursor dispersity are also of interest. Analysis of such data can give an information about structure of agglomerates forming in powders which may become a subject of an independent research.

## ACKNOWLEDGEMENTS

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