

INFLUENCE OF SURFACTANTS ON THE MICROSTRUCTURE OF DENTAL ZIRCONIA CERAMICS

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1. Introduction

Ceramics on the base of tetragonal zirconia ($t\text{-ZrO}_2$) possess high wear and performance strength, resistance to heat and brittle fracture. Excellent biocompatibility enables to spread this ceramics from functional construction materials up to the dental application. Improving the stability of the tetragonal phase of ZrO_2 (the latter is responsible for its high plasticity), is related with sintering ceramics from nanopowder [1-3].

One of the major advantages of using nanopowder in ceramic technology is the intensification of the sintering process. However, the advantages of the size factor are lost in practice due to the fact that nanoparticles, having a high surface free energy, are converted to complex hierarchical system of very large agglomerates. The effective way to reduce the precursor agglomeration during the sol-gel process is the creation of spatial constraints for particle condensation by introducing the surface-active agents (surfactants) [4,5].

This work studies the influence of different surfactants included in the synthesis of precursor powders on the microstructure of ceramic material to search for an optimal agents providing an uniform grain microstructure required for accurate medical products with a high degree of surface cleanliness.

2. Experimental Details

The composition of $98\%\text{ZrO}_2 - 2\%\text{Yb}_2\text{O}_3$ was taken for sol-gel process, which allows to produce powder with the tetragonal crystalline phase of ZrO_2 [2,3]. The sol-gel process was carried out in the presence of the next surfactants in an amount of 0.1% (wt.) of ZrO_2 sufficient to form a mono-or poly-layer on the particle surface [6]:

1. Polyvinyl alcohol (PVA)
2. Polyvinylpyrrolidone (PVP)
3. Starch
4. Without surfactant

Accordingly, the designation of powders was 1, 2, 3 and 4.

The powders were obtained after heating xerogel in the electric furnace at a final temperature of 950°C . The phase composition of the powder was determined by a diffractometer XRD-6000 with emission in the angular range $2\theta = 24\text{-}78^\circ$ and with the identification of the Bank for International Standards (JCPDS).

The method of low temperature adsorption (adsorption-structure analyzer «TriStar - 3000») was applied to measure the specific surface area of the powder. A laser analyzer

«Annalizette-22» was used to determine the size distribution of the agglomerates in the synthesized powders.

Ceramic samples were sintered from *t*-ZrO₂ powders at 1500°C. Their designation corresponds to the marking powder. The investigation of surface microstructure of ceramic samples was carried out by scanning electron microscope (SEM) «LEO 1420» and atomic force microscope (AFM) «NEXT».

3. Results

Diffraction patterns of the powders № 1-4 obtained after heating the precursors at 950° C showed the presence of one crystalline phase - a solid solution on the basis of tetragonal zirconia (*t*-ZrO₂). Fig. 1 illustrates the general view of the powder diffraction patterns in the area of major reflections corresponding to the phase of *t*-ZrO₂ [2,3].

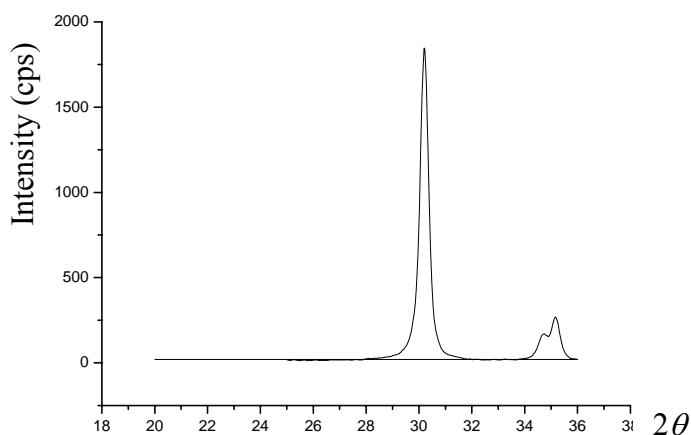


Fig. 1. A fragment of a diffraction pattern of the powder number 1.

The powders have high dispersibility, as shown in the Table 1, the individual particle sizes are within the range of 45 - 70 nm.

Tab. 1. Dimensional characteristics of powders

N	950°C	
	S, m ² /g	D, nm
1	16	60
2	20	45
3	16	60
4	14	70
∇	±1	±1

Size distribution of the agglomerates in the synthesized powders are presented in the Fig.2. All the powders discerned polymodal distribution of agglomerates with inhomogeneous fractional composition.

The maximal content of large (50-150 μm) agglomerates is observed in the powder obtained without surfactants. Agglomerates with sizes from 10 to 30 microns prevail in the samples N2 (obtained with PVP) and we don't find here the big (~100 μm) ones. The size of agglomerates in samples N3 (with starch) range from 10 to 40 microns. Addition of PVA during the sol-gel process (sample N1) gives the agglomerates with size from 10 to 50 microns. All powders reveal also small agglomerates with size from 0.1 to 5 microns.

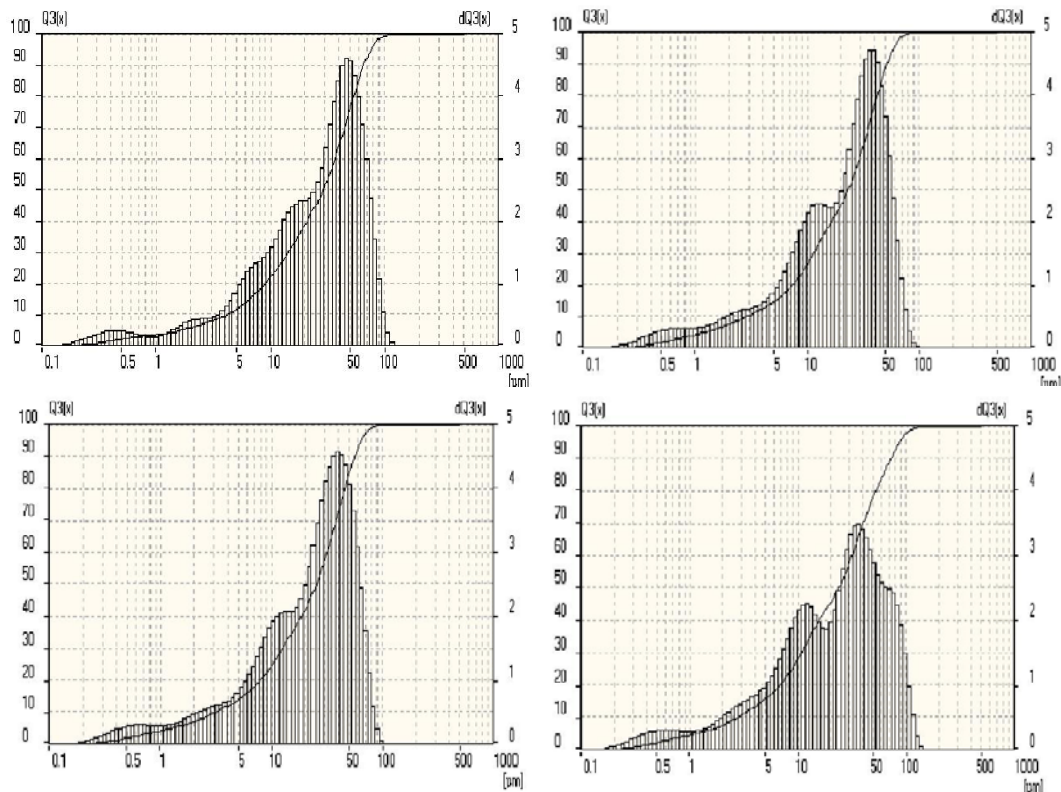


Fig.2. Integral and differential dependence of the distribution of the agglomerate size in the synthesized powders 1,2,3 and 4.

Addition of different surfactants during the sol-gel process affects not only on size of agglomerates in the powder, but also on the microstructure of the sintered ceramics. SEM- and AFM-images of all the samples reveal the grains with a size mostly 0.3 – 1 μm and a few big grains originated from the large agglomerates present in the powder. Since the substructure of the grains affects the strength of the material, it is important to determine its presence or absence. However, it is difficult to make out the inner structure of the grains in the SEM-image but it is good visible in the AFM image (Fig.3). Large grains are presented here as the dense associations occurring in the synthesis step of precursors and may be explained by melting of precursor's agglomerate.

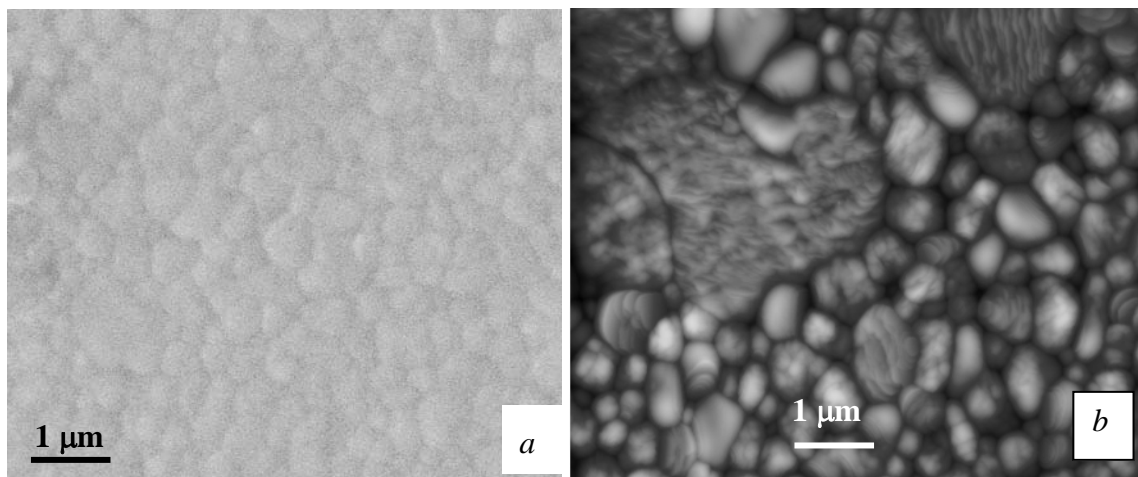


Fig.3. SEM-image (a) and AFM image (b) of the sample 3

At the same time the microstructure of the sample N1 contains the large clusters of small (~300-500 nm) grains (Fig.4 *a*) which originate most likely due to insufficient amount of input surfactant at sol-gel process. The analogous clusters were not observed for sample N2 (Fig.4 *b*) (the white areas here correspond to surface imperfections).

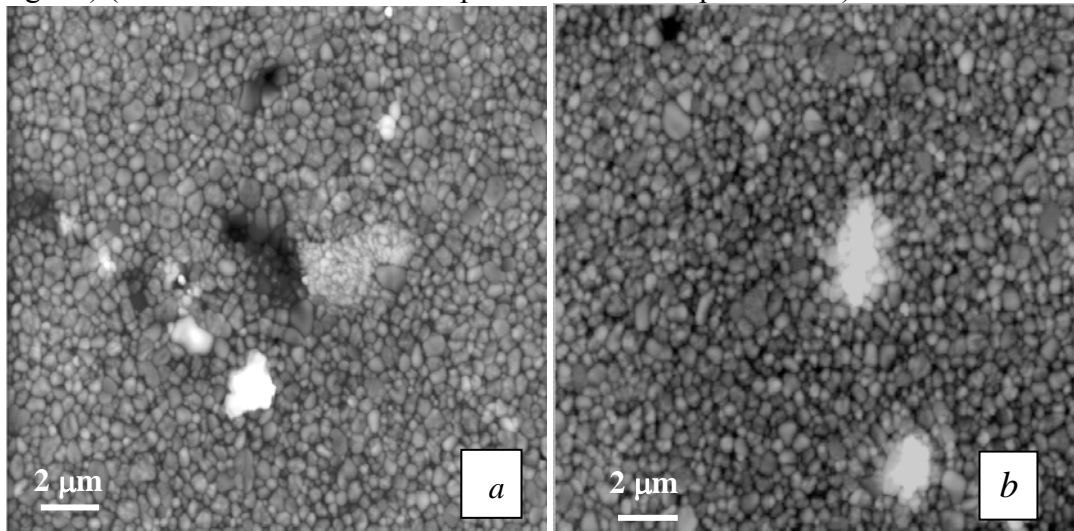


Fig.4. AFM images of the samples N 1(*a*) and N2 (*b*)

4. Conclusion

It was shown that nanopowders of *t*-ZrO₂ are discerned by size distribution of agglomerates, which depends on the added surfactants during sol-gel process. AFM-images show the submicron structure of sintered materials. They reveal also big grains originated most likely from agglomerates of precursors and big agglomerates of submicron grains as well. The results of atomic force microscopy show that the use of surfactants in the form of PVP may provide materials with more uniform grain microstructure.

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