

ZIRCONIA NANOPARTICLES AND CERAMICS: KINETIC OF ISOTHERMAL GROWTH

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Abstract: It is known that the formation of oxide nanopowders takes place in the complex process including as non-isothermal and isothermal stages. In case of powders isothermal heat treatment led to realization of sequential process at transition from amorphous state to crystalline state, in particular, dehydration, crystallization, disintegration of linked nanoparticles in amorphous matrix and ensuing growth of crystals. In this work the questions of forming of particles and ceramic based on these nanoparticles are discussed. The influence of particles characteristics which synthesized at different temperatures on kinetics of isothermal sintering is estimated. It was shown that particles size and surface characteristics influence on kind of diffusion which is realized at ceramic sintering. The possible mechanisms of isothermal stage of nanoparticles and ceramics forming are discussed.

Keywords: OXIDE NANOPOWDERS, SYNTHESIS METHODS, ISOTHERMAL GROWS, DIFFUSION, SINTERING.

1. Introduction

Modern industry actively uses ceramic nanomaterials in the biomedical area, including prosthetics, implantation, as well as technical direction [1-3]. Modernization of metallurgical, engineering and chemical industries require replacement of major metal parts of devices to parts made from ceramic materials, including nozzles, pistons, bearings that are more effective in terms of corrosion resistance [4]. Improving the quality of life lead to the introduction of new standards in medicine, in particular, the development of new ceramic materials, in particular for dentistry, bones recovering, etc., which are biologically inert relative to the human body [5]. Oxide nanomaterials based on zirconium dioxide are the most attractive for these applications [6], however, the nanosized state of the oxide materials is blocked the rapid advancement of such materials on the market. The main reasons for this are the difficulty of working with nanopowders, both during the synthesis of fine-powder and in their further consolidation. Therefore, understanding the processes of nanoparticles synthesis and consolidation are very useful for the successful implementation powders and ceramic products in modern industry.

The most common industrial method of synthesis of nanopowders is precipitation method because it allows synthesized as single, double and multicomponent oxide powders. However, it should be noted that the synthesis of nanoparticles obtained by coprecipitation technology, runs in conditions of temperature processing. Formation of nanoparticles undergo to a set of processes - dehydration, dehydrogenation, degradation and crystallization under the influence of temperature. During the increasing of temperature the processes of nanoparticles growth, surface formation, creation and annealing of anionic and cationic vacancies, a transition from amorphous to crystalline state are occurred [7]. Usually the temperature range of heat treatment is in the range from crystallization temperature to 1200°C.

Increasing temperature leads to an increasing of nanoparticles size and increase their bulk weight, which is important for powders compaction. The formation of tetragonal phase in zirconia nanoparticles is more attractive to the ceramic technology. Obtaining of tetragonal phase in zirconia at room temperature is possible by reducing the size of nanoparticles [8] or by creating the surface defects [9], or mesoporous materials [10]. However, these factors do not to stabilize of zirconium dioxide during change of thermodynamic conditions (temperature, pressure, environment conditions) in time their exploitation. At the same time, the most common method of stabilization of zirconium dioxide nanoparticles in the tetragonal phase is the doping of zirconia lattice by two- or trivalent ions [11-13]. This process allows to stabilize the tetragonal state, make the surface of nanoparticles more active to sintering and to reduce the probability of martensitic tetragonal-monoclinic transition during cooling powders from higher temperatures higher

than 1100°C. Durability of ceramic materials can be increased by varying the type or amount of dopants [14-15]. At the same time, the increasing of ceramics durability due to the structure of ceramics and ability to structure changing [16], which can be varied as type of dopant [17], structural features of powders [18] or sintering regimes [19].

Thus, the potential consumers are forming the requirements to zirconia nanopowders and products thereof. However, no single criterion by which you can choose the best powder, because in order to adapt the functional properties of nanoparticles for specific experimental tasks necessary to understanding the fundamental processes of nucleation and growth of nanoparticles.

2. Experimental

2.1. Material preparation

ZrO₂-3mol% Y₂O₃ (3Y-TZP) nanopowders were synthesized with a co-precipitation technique using ZrOCl₂·nH₂O, Y(NO₃)₃·nH₂O. All used chemicals were of chemical purity. The technological aspects of the precipitation process were described in [20, 21]. After washing and filtration, the hydrogel was dried in a microwave furnace with an output power of 700 W and at a frequency of 2.45 GHz. The dried zirconium hydroxides and composites were calcined in a resistive furnace at temperatures 500, 700 and 1000°C with a dwelling time of 1, 2 and 3h for producing nanopowders with different particle sizes.

2.2. Materials characterization

The powders obtained after calcination were characterized by X-ray diffraction (XRD) employing a Dron-3 diffractometer with Cu-Kα radiation. The region of 2θ-33° was studied in order to determine the volume fraction of the monoclinic phase by a proven method [22]. Data in the angular region of 71°-77° were used to identify the splitting of the (400)_t and (004)_t peaks of the tetragonal phase. Fitting and analysis of the XRD curves was done by Powder Cell software for Windows version 2.4. Coarse α-Al₂O₃ powder was used to measure the instrumental broadening in order to correct the value of line broadening. The Scherer equation was used to determine the average size of the coherent scattering area. The powders were also studied by TEM (Jem 200 A JEOL) and the observed average particle size was compared with the value obtained from XRD. Reliable data were obtained by analysing data from 30 TEM fields for both powders. When a match for XRD data with the results of electron microscopy was found, the size of the primary crystallites could be determined. Our previous work [23] shows non-conformity in particle size determined by X-ray analysis and TEM for certain special modes of heat treatment, but in this work such features will not be considered. Specific surface area of nanopowders was measured using BET method on SORBI-2 instrument [24].

The 3Y-TZP nanopowders with different particles sizes were pressed uniaxially under 50 MPa. The specimen's sizes were 8 mm x15 mm. The shrinkage of the green compacts with sintering was measured using a dilatometer (DIL 402 PC, Netzch, Germany). The shrinkage was measured as a function of time at the constant temperature from 950 to 1400°C. The regimes of sintering at 1300 and 1400°C were chosen because these temperatures often used in large industrial furnaces, for example JSC "KDZ", Ukraine. The dilatometer was calibrated using Al₂O₃ as a standard specimen. Using the thermal expansion coefficient of Y-TZP thermal expansions of the specimens were corrected from the observed shrinkages.

3. Results and discussion

The TEM images of calcined zirconia powder are shown in Figure 1. The XRD analysis shown that the main crystalline phase was a tetragonal - P4m2 type (cards 17-923, 14-534). The XRD and TEM data found that primary 3Y-TZP particles size increased with increasing calcining temperature. The average particle sizes are 13, 19 and 32nm for temperatures of 500, 700 and 1000°C, respectively (Fig.1, Table 1) and decreased slowly with increasing of dwelling time. This process is linked with decreasing of specific surface area.

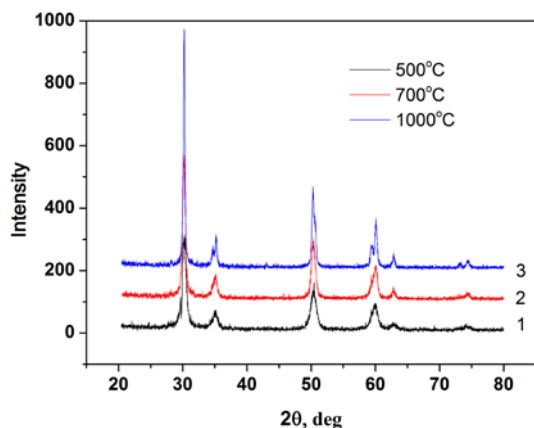


Fig.1 XRD data of 3Y-TZP nanopowders calcined at 500 – 1, 700 – 2 and 1000°C – 3.

Table 1 Dependences of specific surface area and particles size (XRD) from calcination regimes

T°C	S _{sa} , m ² /g			D, nm		
	1h	2h	3h	1h	2h	3h
500	92,4±1,8	87,1±1,1	79,8±1,7	13±0.4	13±0.4	14±0.5
700	50,3±0,6	48,5±0,7	47,9±0,5	19±0.6	20±0.7	21±0.7
1000	21,5±0,3	17,7±0,2	16,2±0,2	32±0.9	35±0.9	37±1.0

In case of nanopowders, calcined at 500 and 1000°C, the strong agglomeration of nanoparticles was observed by TEM, instead of separated nanoparticles, which was observed after calcination at 700°C. The agglomeration processes in nanopowders calcined at 500 and 1000°C due to the different reasons. The Van der Waals forces in first case and starting the sintering processes in second case are the reasons for agglomeration of nanoparticles. But the increasing of dwelling time did not lead to particle agglomeration (Fig. 2).

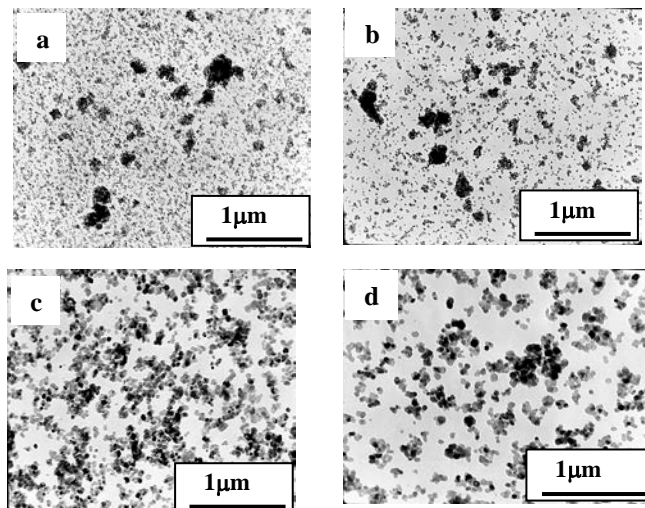


Fig.2 TEM images of 3Y-TZP nanopowders, calcined at 700 a), b) and 900°C – c), d) with dwelling time 1h – a), c) and 3 h – b), d).

The behavior of nanopowders under isothermal heating was studied on nanopowders with different mean particle sizes during heating at 950, 1000, 1050, 1100, 1300 and 1400°C. Figure 3 shows the typical change of fractional shrinkage with heating time at a constant temperature of 1300 and 1400°C.

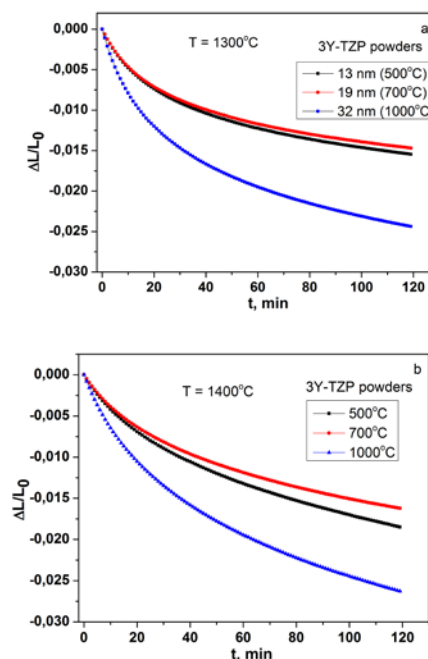


Fig. 3 Change of shrinkage with heating time of 3Y-TZP nanopowders with 13, 19 and 32 nm mean particles size at 1300 and 1400°C. □

When the heating time increased, the fractional shrinkage of 32 nm nanopowders was greater than that of 13 and 19 nm nanopowders. It should be noted that the shrinkage of 19 nm nanopowder is least of all, so dependence of powders shrinkage is nonmonotonic with particle size. The sintering-rate equation of isothermal shrinkage at the initial sintering step is as follows [25]:

$$\frac{\Delta L}{L_0} = kt^n \tag{1}$$

$$\log\left(\frac{\Delta L}{L_0}\right) = n \log t + \log k, \tag{2}$$

where *k* is a numerical constant, which depend on temperature and powder characteristics, *n* is the order depending on the diffusion mechanism.

To apply Eq. (2) to the above results, the isothermal shrinkage curves converted to log–log plots, and the n values of powders shrinkage were determined from the slopes of the straight lines. The n values of 3Y-TZP powders were shown in Table 2.

Table 2 Parameters that determine the rate of sintering at different temperatures.

T, °C	1400°C		1300°C	
	k	n	k	n
500 (13 HM)	0,0013	0,53	0,0015	0,41
700 (19 HM)	0,0015	0,47	0,0029	0,43
1000 (32 HM)	0,0021	0,49	0,0028	0,4

According to two-sphere shrinkage models proposed by several researchers, it has been reported that the n value ranges of grain boundary diffusion (GBD) and volume diffusion (VD) were of n 0.31–0.33 and 0.40–0.50, respectively [25]. Compared with the above n values determined experimentally, it was confirmed that the diffusion mechanisms of studied nanopowders are determined by VD.

However, the powders (for example with an annealing temperature 500 and 700°C) with different powders morphology, having the near n values. This is an interesting question and can be explained by the heterogeneity of the structure of compacted powders. During sintering of inhomogeneous structures in the agglomerates can already be realized mode of volume diffusion between particles, whereas in the rest of the system can be sintered in the regime of grain boundary diffusion. In some time the grain grows also occurred and the determination of n is not true. For the description of the mechanism of sintering in this case, the sintering with constant heating rate should be use.

Conclusion

It was shown the grain growth takes place at heat-treatment of NPs and their compacts. For case in ceramic creation (high temperatures, in our work 1300-1400°C) the process of grain growth takes place due to volume diffusion. For NPs growth this process is complex and is depending on temperature region in which NPs heats. At low temperatures up to 700°C process can include stages of destruction of initial hydroxide matrix at crystallization, creation and annealing of oxygen vacancies, removing of residual ions, hydroxyls and water and other diffusion processes. The growth of NPs in this temperature region is slowly. In temperatures above 700°C the diffusion as anionic and cationic processes begin and growth of NPs is accelerated.

Acknowledgments

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