

# EFFECT OF THE PARTICLE SURFACE ACTIVATION ON THE SINTERING KINETICS OF ZIRCONIA BASED NANOPOWDERS.

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**Abstract.** *In the present study authors examined the sintering behavior on the initial sintering stage of fine tetragonal zirconia nanopowders (containing 3 mol %  $Y_2O_3$ ) with and without mechanical activation in a ball mill. The initial sintering behavior was examined by constant rate of heating method (CRH) at different heating rates. We defined a role of the particles surface mechanical activation and its influence on the sintering mechanisms during the sintering of yttrium-stabilized zirconia nanopowders. We found that even a small mechanical action causes change initial characteristics of nanopowders which can accelerate sintering processes. Increases of milling time causes change of sintering mechanism from volume (VD) to the grain-boundary (GBD).*

**KEYWORDS:** TETRAGONAL ZIRCONIA NANOPOWDER, SINTERING MECHANISM, CONSTANT RATE OF HEATING METHOD (CRH), MECHANICAL ACTIVATION.

## 1. Introduction

Yttria-stabilized tetragonal zirconia (Y-TZP) ceramic is one of the most famous ceramic materials. It is especially applied in biomedical area, in machine and aerospace industry because of higher fracture toughness and strength. Presently actual problems at manufacturing products of zirconia nanopowders are the optimization of the conditions and methods for obtaining nanopowders and their consolidation during sintering. Also of interest are research on extending shelf life of raw materials and improving the quality of ceramics produced from it.

Sintering is one of the most important stages of the formation of nanopowders microstructure. The mechanical properties strongly depend on the microstructure of zirconia based nanoceramics, which can be controlled by applying the sintering-acceleration effect of the mechanical activation, various dopants additives, ultrasonic action, particle surface modification and etc. Optimization of production processes (lowering the sintering temperature and reducing the isothermal hold) nanopowders based on zirconia will increase the production on an industrial scale and to reduce the cost of zirconia ceramics.

In the present study we investigated sintering kinetic of zirconia based nanopowders on the initial sintering stage with and without mechanical activation in a planetary mill.

The main goal of this paper is to investigate the influence of different nanopowders obtaining conditions and on peculiarities of sintering process of ceramics nanocomposites based on yttria-stabilized zirconia. It is especially important to clarify the effect of mechanical milling on sintering process that give able to control the sintering rate of yttria-stabilized zirconia ceramics for producing new ceramic nanocomposites. Mechanical methods of the activation of materials are currently widely used for manufacturing ceramic nanopowders. Intensive milling of ultra-fine and nanometer-sized powders is considered to be a way of applying mechanical activation that involves dispersion of solids, generation and migration of defects in the bulk and plastic deformation of particles [1]. Mechanical activation in ball mill causes decrease grain size and agglomeration degree and this leads to improving forming nanopowders and the acceleration of sintering zirconia based ceramics.

## 2. Experimental procedure

In this paper we use two kinds nanopowders: the nanopowders 3Y-TZP (DIPE) preparation technique consists from next stages:  $ZrOCl_2 \cdot 8H_2O$ ,  $YCl_3$  → co-precipitation method → drying → calcinations → wet mechanical milling (2 min; 8 hours) → we have obtained three kinds of powder: 3Y-TZP (without milling); 02M-3Y-TZP (with milling 2 min); 8M-3Y-TZP (with milling 8 hours).

The second kind of nanopowder is TZ-3Y (Tosoh, Tokyo, Japan) containing 3 mol %  $Y_2O_3$  manufactured by hydrolysis method and 3Y-TZP containing 3 mol%  $Y_2O_3$  (DIPE of the NASU, Ukraine) produced by co-precipitation method.

The preparation TZ-3Y (Tosoh) technique according to the manufactures data consists of several stages:  $ZrOCl_2 \cdot 8H_2O$ ,  $YCl_3$  → technical hydrolysis process → drying → calcinations → mechanical milling (48 hours) → spray-drying (hot gas) → nanopowder TZ-3Y (Tosoh).

All used chemicals have of chemical purity chemical purity. At first appropriate amounts of  $Y_2O_3$  were dissolved in nitric acid; then, the zirconium and yttrium salts were mixed via a propeller stirrer for 30 min and were subsequently added to an aqueous solution of the precipitant (25%  $NH_4OH$ ) with constant stirring. Sediments were mixed for 1 h at room temperature at a pH of 9. Sediments were then repeatedly washed and filtered with distilled water. For chloride salts, washing was carried out until a negative test for  $Cl^-$  ions obtaining with use a silver nitrate solution. After washing and filtration, the hydrogel was dried in a microwave furnace. The calcination of dried zirconia hydroxides was carried out in resistive furnaces at temperature 1000 °C for 2 h. After that two powders were processed in a vibration mill. Powder 02M-3Y-TZP was milled for 2 minutes and powder 8M-3Y-TZP was milled for 8 hours.

The powders obtained after calcination were characterized by X-ray diffraction (XRD) employing a Dron-3 diffractometer with Cu-K  $\alpha$  radiation. Fitting and analysis of the XRD curves were made by Powder Cell software for Windows version 2.4. The powders were also studied by TEM (Jem 200A, JEOL, Japan) and the observed average particle size was compared with the value obtained by XRD. Reliable data were obtained by analyzing data from 30 TEM fields for both powders.

Further, all powders were uniaxial pressured in metallic die, and obtained the samples with dimensions of 62 mm x 6 mm. There after the powder compacts were treated by a high hydrostatic pressure 300 MPa. For dilatometric investigations were prepared samples with next dimensions: diameter 6 mm, height 15-17 mm.

The shrinkage data of the sintering powder compacts was obtained using a dilatometer (NETZSCH DIL 402 PC). The dilatometer was calibrated using a standard sample of  $Al_2O_3$ . Measurements of shrinkage by the constant rate of heating method were carried out in the range from room temperature to 1500 °C with different heating rates of 2.5<sup>0</sup>, 5<sup>0</sup>, 10<sup>0</sup>, 20 °C/min. Upon reaching the temperature of 1500 °C, the samples were cooled at a constant rate. Determination method of sintering mechanisms with using a constant rate of heating technique (CRH) is applicable to the initial sintering stage. The initial sintering stage is not more than 4% of relative shrinkage. In this temperatures range begin to form and grow interparticle contacts, and grain growth else insignificant. Thermal expansion of each sample was corrected with the cooling curve by the method described in [3]. It was confirmed that the

shrinkage proceeded isotopically. The density of sintered samples was measured using the Archimedes method.

### 3. Analytical method for the determination of the diffusion mechanism on the initial sintering stage applicable for a constant rate of heating data.

The diffusion mechanism and activation energy of diffusion at the initial sintering stage were determined by the same analytical method as that in the papers [2-3, 4, 5, 10]. Assuming isotropic shrinkage to samples, the density  $\rho(T)$  at a given temperature  $T$  is given by the following equation:

$$\rho(T) = \left(\frac{L_f}{L(T)}\right)^3 \rho_f \quad (1)$$

Where  $L_f$  is the final length,  $L(T)$  is the length of the sample at a temperature  $T$ ,  $\rho_f$  is the final density of the sample measured by hydrostatic method. For investigations the relative shrinkage no greater than 4% was selected.

The diffusion mechanism and activation energies were determined by the analytical method described in [5]. Sintering rate on the initial stage of sintering is expressed by the equation which was derived by Frankel and Johnson:

$$\frac{d}{dt} \left[ \left( \frac{\Delta L}{L_0} \right)^{\frac{1}{n}} \right] = \frac{K\gamma \Omega D}{kTa^p} \quad (2)$$

$\Delta L = (L_0 - L)$  is the change in length of the specimen;  $K$  is the numerical constant;  $\Omega$  is the atomic volume;  $D$  is the diffusion coefficient;  $\gamma$  is the surface energy;  $t$  is the time;  $T$  is the temperature;  $k$  is the Boltzmann constant;  $a$  is the particle radius; parameters  $n$  and  $p$  the order depending on diffusion.

$$T \cdot c \frac{d\rho}{dT} = \frac{1}{F(\rho)} \cdot \frac{K\gamma\Omega D}{kTa^p} \cdot \exp\left(\frac{-Q}{RT}\right) \quad (3)$$

From kinetic equation (3) derived by Wang and Raj [3-4] we found activation energy using the slope  $S_1$  of the Arrhenius-type plot of  $\ln[T(dT/dt)(d\rho/dT)]$  against  $1/T$  at the same density, the  $Q$  is expressed as:

$$Q = -RS_1 \quad (4)$$

To define sintering mechanism at the initial stage we used the equations derived by Young and Cutler [5] which is based on the kinetics principles formulated by Frenkel and Johnson [5]. After simplification [6], the model chosen has the form:

$$\frac{\Delta L/L_0}{T} = \text{const} \cdot e^{-\frac{nQ}{RT}} \quad (5)$$

Here,  $\Delta L/L_0$  is the relative shrinkage,  $T$  is the temperature,  $Q$  is the activation energy,  $R$  is the gas constant,  $n$  is the constant in range of 0.31–0.50. According to two-sphere shrinkage models proposed by several researchers, the  $n$  value ranges of grain-boundary diffusion (GBD) and volume diffusion (VD) are 0.31–0.33 and 0.40–0.50, respectively [6]. Using the slope  $S_2$  of Arrhenius-type plot of  $\ln [T^{-2-n} d(\Delta L/L_0)/dT]$  against  $1/T$  we found:

$$nQ = -RS_2 \quad (6)$$

From (4) and (6) we found the order of diffusion mechanism:

$$n = S_2/S_1 \quad (7)$$

## 4. Results and Discussion

Agglomeration degree differs according to the conditions for producing nanopowders. The dependence of the agglomerate size against the time of milling was used to optimize the sintering process. It is known that mills used to optimize the preparation process of powders and allows obtaining nanopowders of very high quality with very low levels nanopowders agglomeration [1].

In this paper we investigate two times (2 min and 8 hours) grinding in the mill to select the best option for accelerating the sintering process on the initial sintering stage.

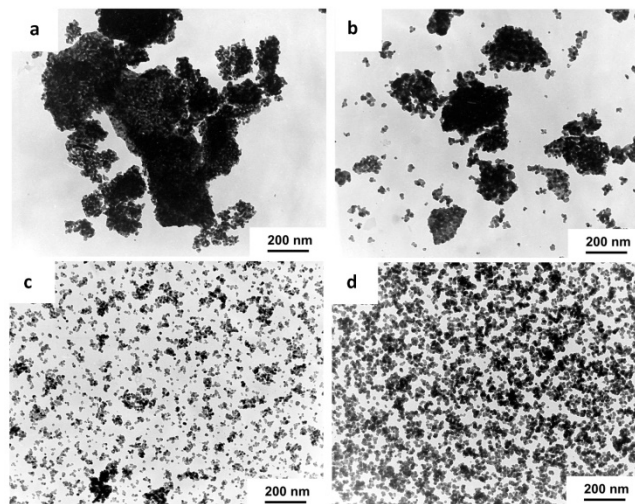


Fig. 1 Transmission electron microscopy (TEM) images of nanopowders structure (a) 3Y-TZP (b); (b) 02M-3Y-TZP; (c) 8M-3Y-TZP; (d) 3Y-TZP TZ-3Y (Tosoh).

As it can be seen from figure 1 the powder (a) 3Y-TZP has a maximum degree of agglomeration in comparison with nanopowders (b) 02M-3Y-TZP and (c) 8M-3Y-TZP and (d) TZ-3Y (Tosoh), which was milling 48 hours. This can be explained by the different duration of milling nanopowders in the mill. It should be noted that agglomerate in 3Y-TZP nanopowder are soft and easily destroyed in under mechanic and high hydrostatic pressure effects ("soft" agglomerates is groups of particles, under the combined action of Van der Waals and easily collapsing under load [1,9]). At eight hours milling in nanopowders (c) 8M-3Y-TZP achieved most homogeneous particle size distribution. Figure 2 shows the TEM images of nanopowders structure: (a) 3Y-TZP; (b) 02M-3Y-TZP; (c) 8M-3Y-TZP and (d) TZ-3Y (Tosoh).

According to the TEM and X-ray diffraction (XRD) data the particle sizes of powders 3Y-TZP and 02M-3Y-TZP are identical  $31.5 \pm 1.5$  nm. The grain size of powder 8M-3Y-TZP is  $25.5 \pm 1.5$  nm which is less than in the powders 3Y-TZP and 02M-3Y-TZP. XRD analysis of powders 3Y-TZP and 02M-3Y-TZP showed the presence of two zirconia crystal lattices: 94% of tetragonal phase and 6% of monoclinic. After 8 hours milling in powder 8M-3Y-TZP, according XRD, the phase composition of the powder was slightly changed: the monoclinic phase percentage was increased up to 18.5%. The grain size of powder TZ-3Y (Tosoh) is  $27.2 \pm 1.4$  nm and the presence of two zirconia crystal lattices: 82% of tetragonal phase and 18% of monoclinic.

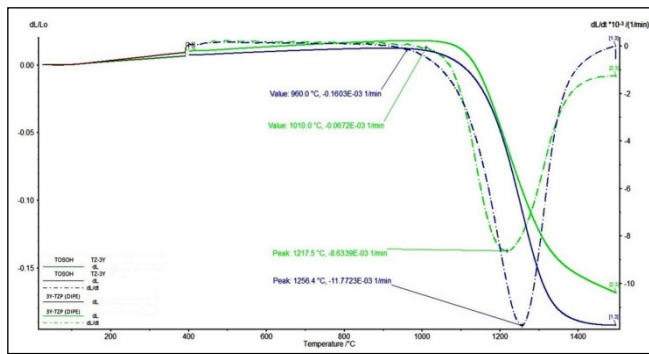


Fig. 2 Temperature dependence of shrinkage and the shrinkage rate for the samples 3Y-TZP, TZ-3Y (Tosoh) at heating rate 10 °C / min.

Figure 2 shows the temperature dependence of the relative shrinkage ( $dL/L_0$ ) and shrinkage rate ( $\Delta L / dt$ ) for the samples 3Y-TZP (DIPE), and TZ-3Y (Tosoh) at a heating rate of 10 °C / min from room temperature to 1500 °C. As can be seen, the onset sintering temperature in samples is different. In the samples TZ-3Y (Tosoh) shrinkage begins earlier at a temperature of 960 °C, and in the sample 3Y-TZP (DIPE) shrinkage begins at 1010 °C. The highest rate of shrinkage is achieved at temperatures of 1171 °C and 1219 °C for 3Y-TZP (DIPE) and TZ-3Y (Tosoh), respectively. It can be seen that the shrinkage of the sample 3Y-TZP (DIPE) is more intense than in the sample TZ-3Y (Tosoh).

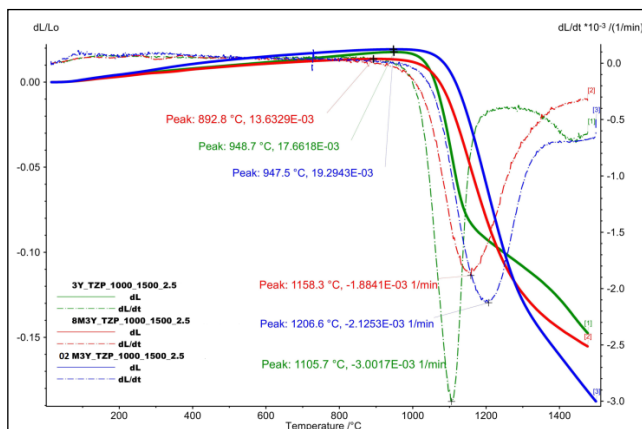


Fig. 3 Temperature dependence of shrinkage and the shrinkage rate for the samples 3Y-TZP, 02M-3Y-TZP, 8M-3Y-TZP at heating rate 2.5 °C / min.

Figure 3 shows the temperature dependence of the relative shrinkage ( $dL/L_0$ ) and shrinkage rate ( $\Delta L/dt$ ) of the samples 3Y-TZP; 02M-3Y-TZP; 8M-3Y-TZP at a heating rate of 2.5 °C / min from room temperature to 1500 °C. As it can be seen, the onset sintering temperatures of shrinkage of these samples is slightly different and shrinkage rate of the sample 3Y-TZP (DIPE) is more intensive than of the other samples.

We think that this difference different of shrinkage rate due to nanopowders obtaining conditions and mechanical activation. As was noted above, nanopowder TZ-3Y (Tosoh) milled in the mill for 48 hours, and nanopowder 3Y-TZP has not been subjected to any mechanical action. This is confirmed by the low agglomeration degree, homogeneous particle size distribution and small grain size of the TZ-3Y (Tosoh) nanopowder, as shown in Figure 1. It should be noted that the mechanical milling in a mill for 8 h gave almost the same effect on the powder 8M-3Y-TZP (Fig.1 (c)), as in TZ-3Y (Tosoh) (Fig.1 (d)).

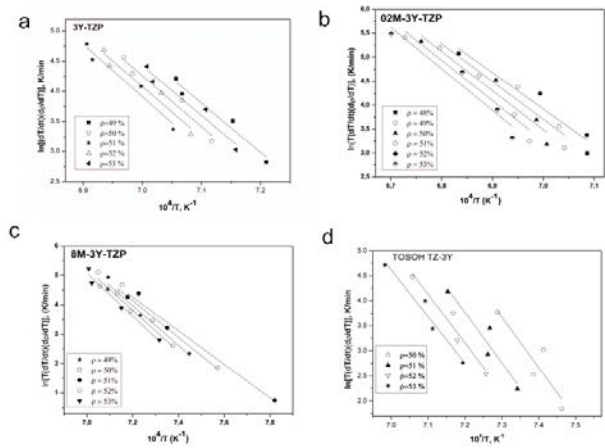


Fig. 4 Arrhenius-type plots of samples (a) 3Y-TZP; (b) 02M-3Y-TZP; (c) 8M-3Y-TZP and (d) TZ-3Y (Tosoh).

The diffusion mechanism of all sintering samples was determined by the method described in articles [2, 4-5] and Arrhenius-type plots presented on figure 4.

Table 1. Activation energy and the order of diffusion mechanisms for the samples 3Y-TZP; 02M-3Y-TZP; 8M-3Y-TZP; 3Y-TZP TZ-3Y (Tosoh).

No	Powders	n	Q, kJ/mol	Sintering mechanism m
1	3Y-TZP	1/2	667±40	VD
2	02M-3Y-TZP	1/2	615±40	VD
3	8M-3Y-TZP	1/3	804±40	GBD
4	TZ-3Y (Tosoh)	1/3	840±40	GBD

The obtained activation energy and the order of diffusion mechanisms ( $n=0.33-0.51$ ) for the samples shown in Table 1. Table 1 show that milling in 2 minutes, does not change the predominate sintering mechanism (mechanism volume diffusion) and milling duration of 8 hours leads to a change the predominant sintering mechanism from volume (VD) to the grain boundary diffusion (GBD). Such change predominant sintering mechanism on the initial sintering stage increases the activation energy of the sintering.

### 5. Conclusions

The present study examined the sintering behavior on the initial sintering stage of tetragonal zirconia nanopowders with and without mechanical activation in a ball mill. The following conclusions were obtained:

1) Milling in a ball mill significant effect on the initial characteristics of powders (agglomeration degree, grain size) and accordingly influence on the kinetics of the initial sintering stage of ceramics. Improving sintering due to milling occurs, apparently, not only by increasing the density of the compacts, but also due increasing defects of the powder particles caused by deformation during densification, which is confirmed by the changing of diffusion mechanism of sintering from volume (VD) in case for nanopowder 3Y-TZP to grain boundary (GBD) in case for 8M-3Y-TZP.

2) We found that even a small milling time (2 min for 02M-3Y-TZP nanopowder), reduces the agglomeration degree and decreases activation energy of sintering at the same time it not change the predominant sintering mechanism.

## 6. Acknowledgments

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## 7. Literature

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