

# THE EFFECT OF SiO<sub>2</sub> ON THE INITIAL SINTERING STAGE OF TETRAGONAL ZIRCONIA NANOPOWDERS.

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**Abstract.** In the present paper authors investigated the effect of 2 wt % SiO<sub>2</sub> addition on the initial sintering stage of tetragonal zirconia nanopowder 3Y-TZP (ZrO<sub>2</sub>-3 mol% Y<sub>2</sub>O<sub>3</sub>) which was manufactured by co-precipitation and mechanical mixing methods. It has been found that small amount SiO<sub>2</sub> has influenced on phase composition, crystallite size and agglomeration degree of zirconia nanopowders. The sintering behavior of 3Y-TZP with and without addition SiO<sub>2</sub> was investigated using the dilatometric data and analytical method for determining the sintering mechanism. The shrinkage behavior of all nanopowders was measured under constant rate of heating (CRH). The sintering mechanism on the initial sintering stage of 3Y-TZP changed from (VD) volume to (GBD) grain boundary diffusion by addition 2 wt% SiO<sub>2</sub> (3Y-TZP+2 wt% SiO<sub>2</sub>) which have manufactured by co-precipitation method. The nanopowder 4PMM-3Y-TZP+2 wt% SiO<sub>2</sub> which has manufactured by mechanical mixing methods sintered according to (VD) volume diffusion mechanism.

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

## 1. Introduction

Zirconia based ceramic materials have gained extensive interests of research. Due to their excellent chemical inertness and mechanical properties, especially the very high fracture toughness, this ceramic material is increasingly considered for a wide range of structural applications such as extrusion dies, cutting tools, valve guides, etc. 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.

Today it is very important to study the influence of the concentration and nature of the additives and their effect on sintering zirconia nanopowders for production unknown properties and new ceramic materials. The initial sintering stage on various ceramic powders has been investigated by many researchers [1-3]. Wang and Raj [4, 5] Young and Cutler [6], have investigated the sintering mechanisms and have estimated the activation energies by the CRH technique. Matsui and al. [1-4] have analyzed initial sintering behavior of 3Y-TZP (Tosoh, Japan) with and without small amount different additives (AlO<sub>2</sub>, GeO<sub>2</sub>, SiO<sub>2</sub>) using the CRH technique, and reported that the sintering mechanism changed from grain boundary diffusion (GBD) to volume diffusion (VD) for all powders. It has been shown remarkably enhancing the densification rate because of a decreasing in the activation energy of sintering. From the industrial standpoint it is really important to clarify how we can control the properties of ceramic based on zirconia microstructures by doping modifying additives.

The major aims of this work are on one hand to obtain a control producing of 3Y-TZP doped SiO<sub>2</sub> ceramic materials, and on the other hand to explore their potential in different applications under certain conditions. The aim requires deep knowledge not only of 3Y-TZP-SiO<sub>2</sub> powders synthesis, compaction and sintering behavior of the composite powders, but also of microstructure evolution during sintering. With this knowledge it is possible to tune the properties of the 3Y-TZP doped SiO<sub>2</sub> through manipulating microstructure by good control of processing or using different processing techniques. Sintering is one of the most important stages of formation nanopowdes microstructure. The mechanical properties strongly depends 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.

In the present paper was investigated sintering kinetics of zirconia based nanopowders 3Y-TZP (DIPE, Ukraine) on the initial

sintering stage with and without mechanical activation of nanopowders in a planetary mill. It was found that the nanopowders synthesis methods significantly affected on sintering kinetics. The initial sintering behavior of 3Y-TZP nanopowders with and without 2 wt % SiO<sub>2</sub> produced by co-precipitation and mechanical mixing methods using the CRH method was investigated.

## 2. Experimental procedure

The starting materials were based on 3 mol% Y<sub>2</sub>O<sub>3</sub> (3Y-TZP) nanopowders which were manufactured co precipitation method in the DIPE, Ukraine. Ceramic nanopowders with 2 wt% SiO<sub>2</sub> were prepared by co precipitation method and by mixing 3Y-TZP together with SiO<sub>2</sub> in planetary mill for 4 hours. Method preparation technique consists from next stages: ZrOCl<sub>2</sub>\*8H<sub>2</sub>O, YCl<sub>3</sub> → co-precipitation method → drying → calcinations → mixing with milling for 4 hours in a planetary mill. We have obtained three kinds of powders:

- 1) 3Y-TZP;
- 2) 3Y-TZP-2 wt% SiO<sub>2</sub> (co-precipitation);
- 3) PMM4-3Y-TZP-2 wt% SiO<sub>2</sub> (mixing with milling 4 hours).

All used chemicals have of chemical purity chemical purity. At first appropriate amounts of Y<sub>2</sub>O<sub>3</sub> 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<sub>4</sub>OH) 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<sup>-</sup> 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 obtained powders after calcination were characterized by X-ray diffraction (XRD) employing a Dron-3 diffractometer with Cu-K α 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  $\text{Al}_2\text{O}_3$  sample. 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>o</sup>, 5<sup>o</sup>, 10<sup>o</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 isotropically. 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.

From kinetic equation (1) derived by Wang and Raj [4-5] we found activation energy Q of sintering using the slope  $S_1$  of the Arrhenius-type plot of  $\ln[T \cdot (dL/dt)(dp/dT)]$  against  $1/T$  at the same density. For investigations the relative shrinkage no greater than 4% was selected.

$$T \cdot c \frac{d\rho}{dT} = \text{const} \cdot e^{\left(\frac{-Q}{RT}\right)}(1)$$

Here  $\rho$  is the density, T is the temperature, c is the heating rate (°C/min), R is the gas constant.

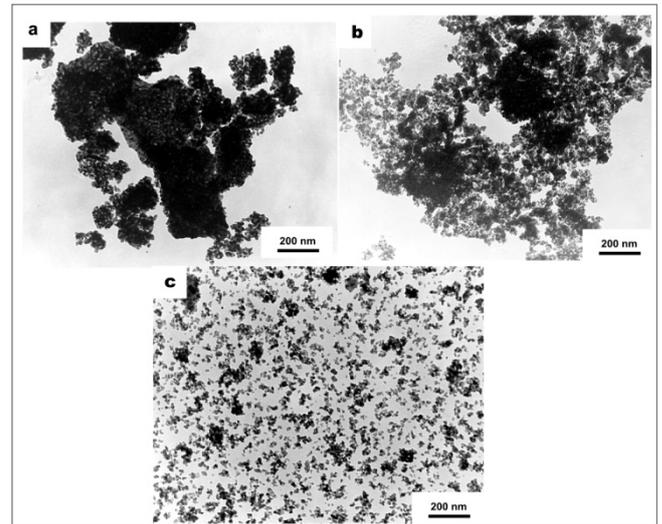
To define sintering mechanism at the initial stage we used the equations derived by Young and Cutler [4] which is based on the kinetics principles formulated by Frenkel and Johnson. After simplification, the chosen model has the form:

$$\frac{\Delta L/L_0}{T} = \text{const} \cdot e^{\left(\frac{-nQ}{RT}\right)}(2)$$

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 (is the order of diffusion mechanisms). 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 [5]. Using the slope  $S_2$  of Arrhenius-type plot of  $\ln [T^{2-n} \cdot d(\Delta L/L_0)/dT]$  against  $1/T$  we found n.

### 4. Results and Discussion

The fig.1 shows dependence of agglomeration degree on the obtaining conditions of nanopowders. On the nanopowders structure influence both factors - the doping way of additives and additive  $\text{SiO}_2$ . The powder (a) 3Y-TZP has a maximum agglomeration degree in comparison with nanopowders (b) Y-TZP-2 wt %  $\text{SiO}_2$  and (c) PMM4-3Y-TZP -2 wt %  $\text{SiO}_2$ .



**Fig. 1** Transmission electron microscopy (TEM) images of nanopowders structure (a) 3Y-TZP (b); (b) 3Y-TZP-2 wt %  $\text{SiO}_2$  (co-precipitation); (c) PMM4-3Y-TZP-2 wt %  $\text{SiO}_2$  (mixing with milling 4 hours).

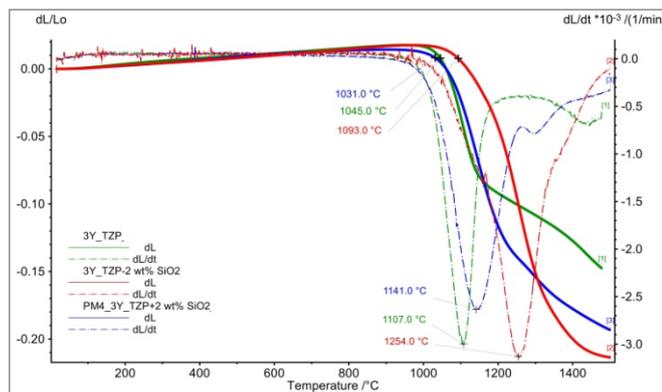
The minimum agglomeration degree and most homogeneous particle size distribution found for PMM4-3Y-TZP -2 wt %  $\text{SiO}_2$  nanopowder. This can be explained by the milling nanopowders in the mill during 4 hours. It should be noted that agglomerate in 3Y-TZP nanopowder are soft and easily destroyed 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).

**Table 1** The nanopowders characteristics

№	Nanopowders composition	Region of coherent scattering, nm	The phase composition, % M-phase
1	3Y-TZP (co-precipitation)	31	5 %M + T
2	3Y-TZP-2 wt % $\text{SiO}_2$ (co-precipitation)	22	100 % T
3	PMM4-3Y-TZP-2 wt % $\text{SiO}_2$ (mixing with milling 4 hours)	27	12 %M+ 88%T

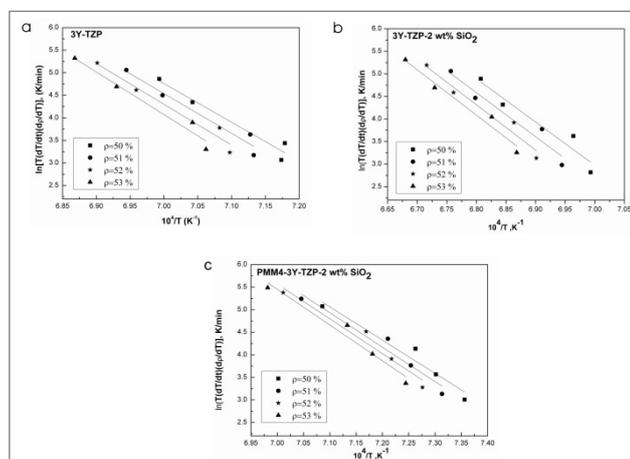
According to the TEM and X-ray diffraction (XRD) data the particle sizes of all nanopowders are different. It can be seen the smallest particle size is 22 nm for 3Y-TZP-2 wt %  $\text{SiO}_2$  nanopowder which was obtained by co-precipitation method. After 4 hours milling of PMM4-3Y-TZP-2 wt%  $\text{SiO}_2$  powder, according XRD, the phase composition of the powder was slightly changed: the monoclinic phase percentage was increased up to 12%. This effect can be explained by the presence of mechanical activation in the production of the nanopowder (c). We can conclude that the  $\text{SiO}_2$  additives significantly affected on nanopowders characteristics.

Figure 2 shows the temperature dependence of the relative shrinkage ( $dL/L_0$ ) and shrinkage rate ( $\Delta L/dt$ ) of the samples 3Y-TZP, 3Y-TZP-2 wt %  $\text{SiO}_2$ , PMM4-3Y-TZP-2 wt %  $\text{SiO}_2$  at a heating rate of 2.5 °C / min on room temperature to 1500 °C. It can be seen, the starting sintering shrinkage temperatures of these samples are slightly different and shrinkage rate of the sample PMM4-3Y-TZP-2 wt %  $\text{SiO}_2$  is more intensive than of the other samples. This difference of shrinkage rate due to mechanical activation nanopowder for 4 hours and 2 wt %  $\text{SiO}_2$  addition. It is confirmed by the low agglomeration degree, homogeneous particle size distribution and small grain size of the PMM4-3Y-TZP-2 wt %  $\text{SiO}_2$  nanopowder, as shown on Figure 1.



**Fig. 2** Temperature dependence of shrinkage and the shrinkage rate for the samples 3Y-TZP, 3Y-TZP-2 wt % SiO<sub>2</sub> (co-precipitation); PMM4-3Y-TZP-2 wt % SiO<sub>2</sub> (mixing with milling 4 hours).

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 3.



**Fig. 3** Arrhenius-type plots of samples (a) 3Y-TZP; (b) 3Y-TZP-2 wt % SiO<sub>2</sub>; (c) PMM4-3Y-TZP-2 wt % SiO<sub>2</sub>.

The activation energy and the order of diffusion mechanisms for the samples have shown in Table 2. According to the results on figure 2 the sintering rate increases with addition SiO<sub>2</sub> by mechanical mixing method. This result shows that the diffusion mechanism did not change from volume diffusion but significantly reduced the activation energy of sintering. This effect is caused by a complex influence additive and mechanical activation of nanopowder.

**Table 2** Activation energy and the order of diffusion mechanisms for the samples 3Y-TZP, 3Y-TZP-2 wt % SiO<sub>2</sub>, PMM4-3Y-TZP-2 wt % SiO<sub>2</sub>.

No	Powders	n	Q, kJ/mol	Sintering mechanism
1	3Y-TZP	1/2	667±40	Volume diffusion (VD)
2	3Y-TZP-2 wt % SiO <sub>2</sub>	1/3	757±40	Grain boundary diffusion (GBD)
3	PMM4-3Y-TZP-2 wt % SiO <sub>2</sub>	1/2	660±40	Volume diffusion (VD)

The SiO<sub>2</sub> addition by co-precipitation method leads to a change the predominant sintering mechanism from volume (VD) in case 3Y-TZP to the grain boundary diffusion (GBD) in case 3Y-TZP-2 wt % SiO<sub>2</sub> nanopowder. Such change predominant sintering mechanism on the initial sintering stage increases the activation energy of the sintering as shown in table 1.

## 5. Conclusions

The present study examined the sintering behavior on the initial sintering stage of tetragonal zirconia nanopowders with (3Y-TZP-2 wt % SiO<sub>2</sub>) and without (3Y-TZP) addition 2 wt% SiO<sub>2</sub>; with (PMM4-3Y-TZP-2 wt % SiO<sub>2</sub>) and without (3Y-TZP-2 wt % SiO<sub>2</sub>) mechanical activation in a planetary mill. It was found the 3Y-TZP nanopowder (without additives and milling) was sintered by the volume diffusion mechanism. The 3Y-TZP-2 wt % SiO<sub>2</sub> (co-precipitation) was sintered by the grain boundary diffusion mechanism. The changing sintering mechanism from VD to GBD which accompanied increasing activation energy of sintering from 667 to 757 kJ/mol is due to influence of 2 wt% SiO<sub>2</sub> addition.

In case PMM4-3Y-TZP-2 wt % SiO<sub>2</sub> nanopowder which was obtained by mixing and milling we found significant effect of two factors: SiO<sub>2</sub> addition and milling on the initial characteristics of nanopowder: agglomeration degree, grain size, phase composition. This two factors also effect on the kinetics of the initial sintering stage of tetragonal zirconia ceramics. The nanopowders PMM4-3Y-TZP-2 wt % SiO<sub>2</sub> was sintered with the highest sintering rate (in comparison with two other nanopowders) at lowest activation energy 660 kJ/mol by the volume diffusion mechanism.

## 6. Acknowledgments

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## 7. Literature

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