

THE EFFECT OF ZIRCONIA NANOPOWDERS' STRUCTURE MODIFICATION BY GeO₂ ADDITION ON THE KINETICS OF THE INITIAL SINTERING STAGE

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Abstract

The impact of GeO₂ on the sintering kinetics and mass transfer mechanisms in tetragonal zirconia nanopowders has been investigated. The shrinkage kinetics of 3Y-TZP was investigated by the dilatometry analyses. The constant rate of heating method was used to determine the dominant mass transfer mechanisms at the initial sintering stage. It was found that GeO₂ in depends on the synthesis method and its amount caused the viscous flow mechanism participation at the initial sintering stage. The sintering mechanism in co-precipitated 3Y-TZP-GeO₂ powders was changed from volume diffusion mechanism to the volume diffusion with viscous flow mechanism. In mixed 3Y-TZP-GeO₂ powders, the sintering mechanism changed from grain boundary diffusion to the volume diffusion with viscous flow mechanism participation. In both types of nanopowders such sintering mechanism changing leads to the activation energy of sintering decreasing that reduces a sintering temperature and activates the densification process in 3Y-TZP.

Keywords: Zirconia, nanopowders, nanocomposites, sintering, additives

1. INTRODUCTION

Tetragonal zirconia (Y-TZP) ceramics is commercially very significant material, which used as an anode material in SOFCs, as a catalyst oxygen sensor and structural, medicine materials because of its physical and mechanical properties such as: high strength and fracture toughness, chemical and radiation resistance, ionic conductivity, biocompatibility, etc. [1]. It is known that ceramics properties strongly depend on the powders structure, thus, it is necessary to control the characteristics of nanoparticles' structure such as particle size, porosity, density, agglomeration degree, surface properties etc. [2-3]. Ceramic materials with improved physical and mechanical properties can be obtained by doping of 3Y-TZP with different additives. Matsui, Sakka and Suarez have reported that low amounts of Al₂O₃ lead to an increase in the strength and hardness of the zirconia ceramic [4-6]. GeO₂ and SiO₂ cause a super plasticity of the sintered material, the addition of NiO is used to create of solid oxide fuel cells [1]. Regarding the production of nanoparticles with given properties, not only doping by additives but also synthesis conditions have a great effect which leads to the powders structure modifying as was shown in our previous studies [7-9]. Additives can form solid solutions in zirconia lattice [1,3]. In addition, dopants create different defects and active centers on the particles' surface, which caused significant changes in nanopowders characteristics [2-3]. Zirconia nanopowders structure modifying by dopants influences on the sintering and can effect on the mass transfer mechanisms at the initial sintering stage [1, 4-6]. Different additives influence on the zirconia densification as well as a synthesis conditions in a different way. The sintering can be activated and slow down by dopants addition in depends on synthesis methods and additives amount [2-3]. One of the topical problems of materials science today is zirconia based ceramics with improved properties and activation of its sintering process. The main goal of the present study is to study the effect of GeO₂ addition on the 3Y-TZP nanopowders' structure and investigate influence of GeO₂ on the densification and mass transfer mechanisms at the initial sintering stage.

2. METHODS

For the investigation the nanopowders $ZrO_2+3 \text{ mol\% } Y_2O_3$ (3Y-TZP), 3Y-TZP+ $n \cdot GeO_2$, PMM8-3Y-TZP+ $n \cdot GeO_2$ obtained by co-precipitation and mechanical mixing methods were used. Where n is the additive amount, $n = 0.2, 1, 2, 3, 5 \text{ wt\%}$ and PMM8 marks of mixed and milled for 8 h powders. 3Y-TZP was synthesized using of $ZrOCl_2 \cdot nH_2O$, $Y(NO_3)_3 \cdot nH_2O$ salts. The preparation technique is described in studies [7-9]. After precipitation, the synthesized hydrogels were dried in a microwave furnace with output power of 700 W and at a frequency of 2.45 GHz. The dried hydroxides were calcined in a resistive furnace at 1000 °C with for 2 h. Calcined at 1000 °C for 2 h 3Y-TZP and GeO_2 nanopowders were mixed in the planetary mill (MSK-SFM-1 (MTI Corp., USA) at 400 rpm for 8 h using YSZ milling balls). Thereafter, all nanopowders were pressed at 300 MPa and sintered up to the 1500 °C with different heating rates of 2.5, 5, 10, 20 °C /min in the dilatometer (NETZSCH DIL 402 PC). The shrinkages data of specimens during sintering were measured by dilatometry. Thermal expansion of specimens was corrected with the cooling curve [4-5]. The final density of sintered specimens was measured by the Archimedes method. The lattice parameters, phase compositions and crystallites size of all nanopowders were investigated by X-ray diffraction (XRD) employing the Dron-3 diffractometer with Cu-K α radiation using the Debye-Scherrer equation. Fitting and analysis of the XRD curves were made by Powder Cell. The particles size and powders structures were studied by the transmission electron microscope TEM (Jem 200A, JEOL, Japan). The microstructures of the sintered ceramics were studied by scanning electron microscopy (JSM 6490LV JEOL) after polishing and thermally etching of specimens' surfaces (at 1450 °C for 0.5 h). The standard constant rate of heating (CRH) technique was used to analyze the obtained dilatometric data [4-6]. Using the CRH technique let to identify the sintering parameter n and activation energy of sintering Q . Considering that if $n = 1$, this means that the viscous flow mechanism dominates (VF). If $n = 0.4-0.5$, the volume diffusion mechanism (VD) dominates and if $n = 0.3-0.4$, the grain boundary diffusion mechanism (GBD) dominates [4-6].

3. RESULTS AND DISCUSSION

The characteristics of the 3Y-TZP- GeO_2 nanopowders are shown in the **Table 1**. The XRD spectra of nanopowders 3Y-TZP, 3Y-TZP+2 wt% GeO_2 , PMM8-3Y-TZP+2 wt% GeO_2 synthesized by mixing and co-precipitation techniques are present in the **Figure 1**. GeO_2 additive were not detected as a separate phase in 3Y-TZP as can be seen from the **Figure 1a** (the additive' peak should be situated within 25-27 degree in the XRD pattern). The GeO_2 does not effect on the phase composition of zirconia but 8 hours of milling leads to the monoclinic phase amount increasing up to 15.5 % in the initial PMM8-3Y-TZP and to 25 % in PMM8-3Y-TZP-5 wt% GeO_2 . Crystallites size of all investigated nanopowders decrease and its specific surface area increasing at the same time (**Figure 1b**, **Table 1**).

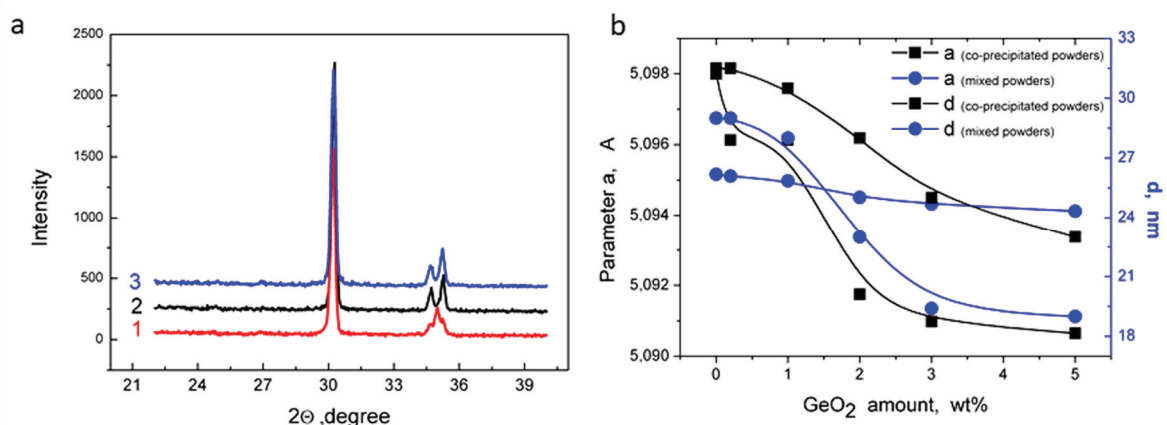


Figure 1 The XRD patterns of nanopowders (a): 1- 3Y-TZP; 2-3Y-TZP-2 wt% GeO_2 ; 3-PMM8-3Y-TZP-2 wt% GeO_2 and (b) the lattice parameters crystallites sizes changing of the investigated nanopowders

Figure 1b shows that GeO₂ has a greater effect on the particles' size and the lattice parameters of zirconia in co-precipitated (black curves) powders than in mechanically mixed powders (blue curves). In the **Figure 2** the nanopowders' structure of co-precipitated and mixed nanopowders are shown. The separate GeO₂ phase was observed in mixed 3Y-TZP-GeO₂ powders (**Figure 2e, f**). Moreover, as was mentioned above the GeO₂ was not detected as a separate phase by XRD in contrast to the mixed powders (**Table 1, Figure 2**). Thus, it can be concluded that in 3Y-TZP-GeO₂ system obtained by co-precipitation was the solid solution GeO₂ with zirconia matrix created because of precipitation. Mixed PMM8-3Y-TZP-GeO₂ powders systems create a two-phase structure (separate phases of GeO₂ and 3Y-TZP). The decrease in the crystallites sizes, for example, from 29 nm to 19 nm in case of PMM8-3Y-TZP-5 wt % GeO₂ nanopowder was caused by milling because the solid solutions were not created in mixed nanopowders (**Figure 1b, Table 1**).

Table 1 The XRD and BET analysis results

Nanopowders composition	% M-phase	Particle size, nm	Lattice parameters, Å	S _{BET} , g/m ³
3Y-TZP	4	31.5	a=5.0980, c=5.17396	14.2
3Y-TZP-0.2 wt % GeO ₂	4	31.5	a=5.09613, c=5.17186	10.2
3Y-TZP-1 wt % GeO ₂	2	30.5	a=5.09613, c=5.16893	11.0
3Y-TZP-2 wt % GeO ₂	1	28	a=5.09175, c=5.1677	14.0
3Y-TZP-3 wt % GeO ₂	1	25	a=5.09065, c=5.16695	16.0
3Y-TZP-5 wt % GeO ₂	0	23	a=5.09065, c=5.16695	19.0
PMM8-3Y-TZP	15.5	29	a=5.095163, c=5.16670	19.9
PMM8-3Y-TZP-0.2 wt % GeO ₂	12	29	a=5.095163, c=5.16670	19.9
PMM8-3Y-TZP-1 wt % GeO ₂	13	28	a=5.095163, c=5.16670	19.7
PMM8-3Y-TZP-2 wt % GeO ₂	22.5	23	a=5.095163, c=5.16670	19.5
PMM8-3Y-TZP-3 wt % GeO ₂	23	19.4	a=5.095163, c=5.16670	19.2
PMM8-3Y-TZP-5 wt % GeO ₂	25	19	a=5.095163, c=5.16670	18.9

M-the monoclinic phase amount, standard deviation of the lattice parameters determination is $\Delta a = \pm 0.0006$, $\Delta c = \pm 0.0005$.

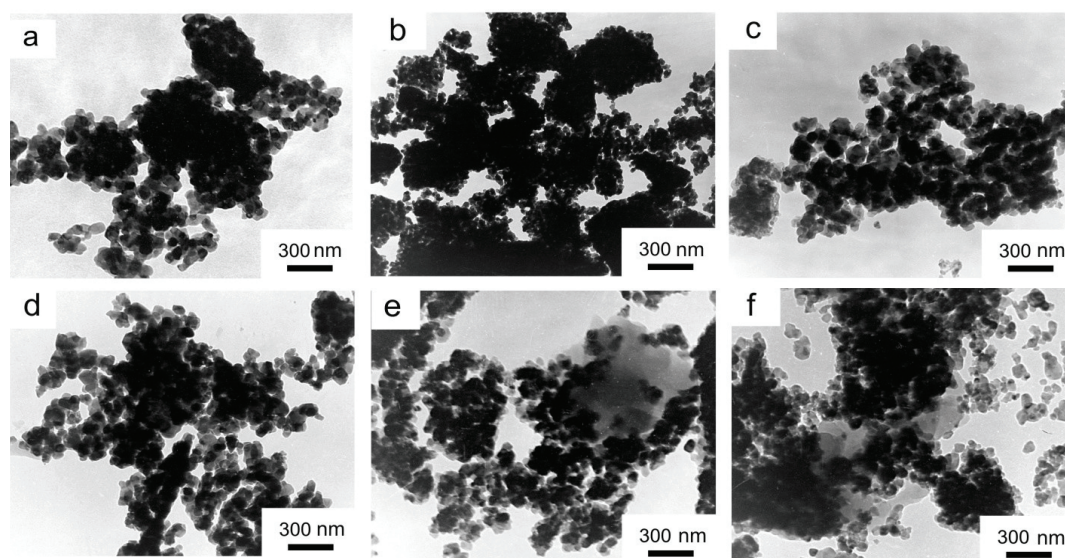


Figure 2 TEM images of nanopowders (a) 3Y-TZP, (b) 3Y-TZP-2 wt% GeO₂, (c) 3Y-TZP-5 wt% GeO₂, (d) PMM8-3Y-TZP, (e) PMM8-3Y-TZP-2 wt% GeO₂, (f) PMM8-3Y-TZP-5 wt% GeO₂

The densification kinetics of 3Y-TZP with 2 wt% GeO₂ specimens obtained by both methods is shown in the **Figure 3a**. As can be seen GeO₂ additive causes the densification rate changing in 3Y-TZP nanopowders. Namely, the temperature value of maximum densification rate (dp/dT) in co-precipitated and mixed 3Y-TZP powders with GeO₂ shifted to smaller values of temperatures (**Figure 3a**). This means that all specimens with GeO₂ were sintered faster than initial 3Y-TZP and PMM8-3Y-TZP powders without additive. Thus, can be concluded that GeO₂ accelerates the sintering of 3Y-TZP.

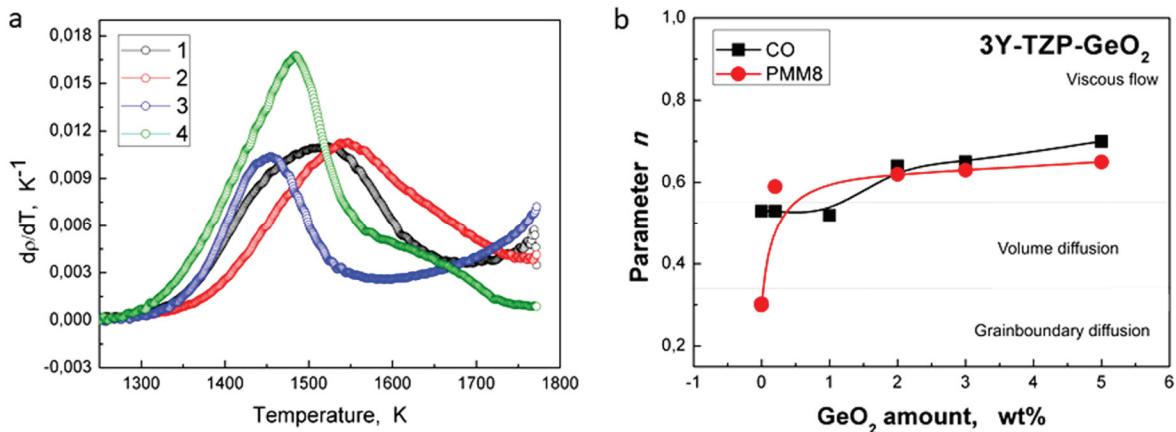


Figure 3 Temperature dependence of densification rate of nanopowders (a): (1) - 3Y- TZP; (2) - PMM8-3Y; (3) - 3Y- TZP -2 wt% GeO₂, (4) - PMM8-3Y- TZP -2 wt% GeO₂ at 10 °C/min and (b) the sintering mechanism changing in 3Y-TZP- GeO₂

The dominant mass transfer mechanism in all investigated specimens at the initial sintering stage has been determined using the CRH technique [4-6]. The **Figure 3b** shows the sintering mechanism changing in all investigated specimens according to the additive amounts and synthesis methods. As can be seen from the **Figure 3b** the co-precipitated 3Y-TZP-GeO₂ specimens were sintered due to the VD mechanism domination. But with additive amount increasing (1-5 wt%) the parameter n tends to 1 and this means that the sintering occurred with the participation of the viscous flow mechanism (VF). The liquid phase effected on the densification of 3Y-TZP-GeO₂ and caused the activation energy of sintering decreasing that led to the sintering process activation.

In mixed PMM8-3Y-TZP-GeO₂ specimens the sintering mechanism changing from GBD to VD with a small amount (0.2 wt%) of GeO₂ addition was observed. Similarly, the parameter n tends to 1 with additive amount increasing (1-5 wt%) and this means that the VF mechanism participates in sintering process too.

The VF mechanism was caused by the low melting point of GeO₂ ($T=1116$ °C) which coincides to the temperatures of the initial stage of sintering. The boiling point of GeO₂ is 1200 °C. Due to these facts, GeO₂ leaves the solid solution with temperature increasing during sintering, activates the VF mechanism and evaporates in co-precipitated powders. The same GeO₂ behavior was observed in mixed nanopowders but the melting and evaporation started earlier since at the beginning of sintering GeO₂ was a separate phase in 3Y-TZP. Based on XRD, TEM, SEM, dilatometry data the scheme of the GeO₂ behavior was build. The scheme and SEM images are shown in the **Figure 4** to confirm the results of investigations and our conclusions.

As can be seen from the **Figure 4** the initial nanopowders states of obtained by different methods were the solid solution (1.1) and two-component mix of 3Y-TZP and GeO₂ (2.1). At the initial sintering stage the solid solution decomposition (1.2, 2.2), melting and evaporation of GeO₂ occur in both types of powders. Because of sintering of different nanopowders types (1.3 and 2.3) the ceramic materials with the single-phase 3Y-TZP structure without GeO₂ was obtained (this confirmed by SEM images at 1200 and 1500 °C as shown in the **Figure 4**).

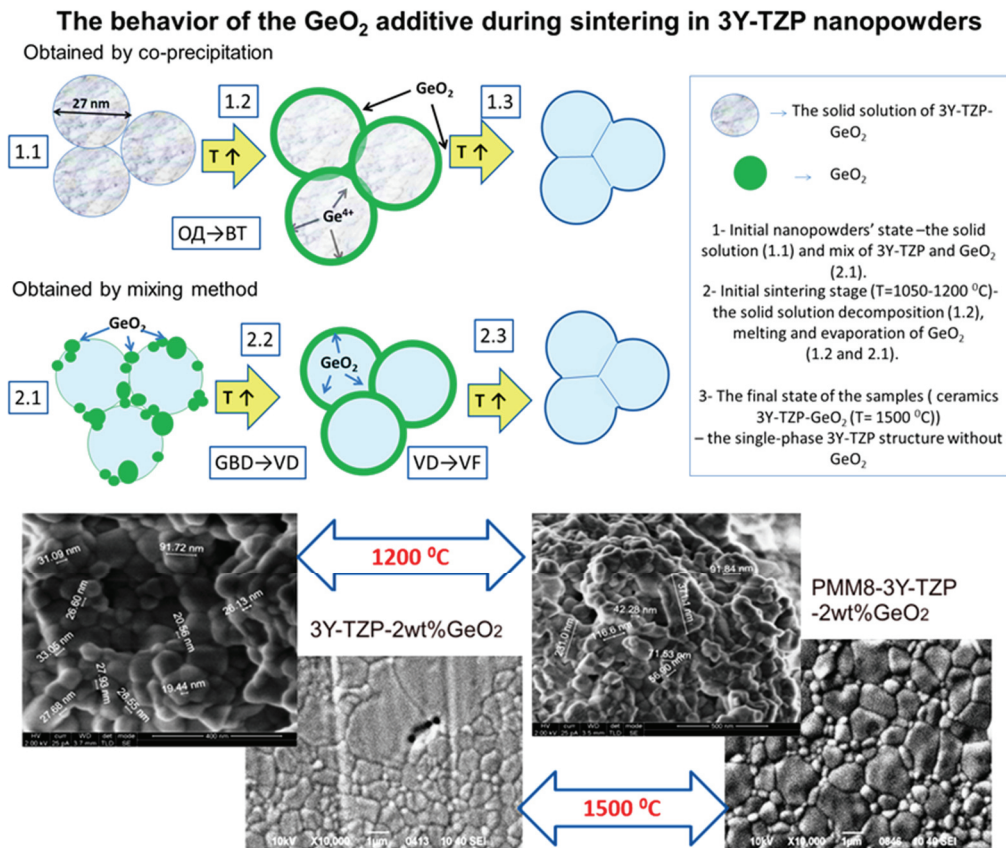


Figure 4 The scheme of GeO₂ behavior during 3Y-TZP sintering and SEM images of 3Y-TZP-2 wt% GeO₂, PMM8-3Y-TZP-2 wt% GeO₂

CONCLUSION

The impact of GeO₂ addition on sintering kinetics of tetragonal zirconia nanopowders has been investigated. The following results were obtained: i) The predominant sintering mechanism in the initial 3Y-TZP prepared by co-precipitation was VD mechanism and GBD in mixed PMM8-3Y-TZP nanopowders; ii) The small amount of the GeO₂ in mixed nanopowders led to the sintering mechanism changing from GBD to VD; iii) The additive amount increasing (1-5 wt%) in both types of powders (3Y-TZP-GeO₂, PMM8-3Y-TZP-GeO₂) caused the participation of the VF mechanism in sintering process. It was found that the GeO₂ accelerated the sintering process and helped create a single-phase 3Y-TZP ceramics with a narrow grain size distribution, which can have the most favorable effect on the properties of obtained ceramic materials for the functional application.

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REFERENCES

- [1] RAGULYA, Andrey V. and SKOROCHOD Volodimir V. *Scientific book: Consolidated nanostructured materials*. Kiev: Naukova Dumka, 2007. p. 499.
- [2] GEGUZIN Jakob E. *Scientific book: Physics of sintering*. Moscow: Science, 1967. p.321.
- [3] KINGERY WD. *Scientific book: Introduction to ceramics*. 3rd ed. Moscow: Stroiizdat, 1967. p.500.

- [4] LAKUSTA, Marharyta, DANILENKO, Igor, KONSTANTINOVA, Tetyana and VOLKOVA, Galina. Influence of Obtaining Conditions on Kinetics of the Initial Sintering Stage of Zirconia Nanopowders. *Nanoscale Research Letters*. 2016. Vol. 11, pp.238-245.
- [5] LAKUSTA, Marharyta, DANILENKO, Igor, KONSTANTINOVA, Tetyana and VOLKOVA, Galina, GORBAN, Oksana. The Effect of a Small Amount SiO₂ on Sintering Kinetics of Tetragonal Zirconia Nanopowders. *Nanoscale Research Letters*. 2017. Vol.12, pp.398-407.
- [6] LAKUSTA, Marharyta, DANILENKO, Igor, KONSTANTINOVA, Tetyana and VOLKOVA, Galina, LOLADZE Larisa, BURCHOVETSKIY, Valeriy. Comparative analyses of the IV group oxides additives influence on the sintering kinetics of zirconia nanopowders. *PLOS ONE*. 2018, pp.1-17. Available from: doi.org/10.1371/journal.pone.0200869.
- [7] MATSUI, Koji. Sintering kinetics at constant rates of heating: effect of GeO₂ addition on the initial sintering stage of 3 mol% Y₂O₃-doped zirconia powder. *J Mater Sci*. 2008. Vol. 43, pp. 852-859.
- [8] MATSUI, Koji. Sintering Kinetics at Constant Rates of Heating: Mechanism of Silica-Enhanced Sintering of Fine Zirconia Powder. *J. Am. Ceram. Soc*. 2008. Vol. 91,8, pp. 2534-2539.
- [9] SUARREZ, Gustavo, SAKKA Yoshio, Effect of alumina addition on initial sintering of cubic ZrO₂ (8YSZ). *Ceramics International*. 2010, Vol. 36. pp. 879-885.