

# BULK ZIRCONIA NANOCERAMICS PREPARED BY COLD ISOSTATIC PRESSING AND PRESSURELESS SINTERING

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**Abstract.** Zirconia nanoparticles (stabilized by 1.5 and 3 mol.% of yttria) with particle size below 10 nm were prepared by a sol-gel synthesis. Isostatically pressed green bodies had pore radii smaller than 5 nm. After pressureless sintering at 1100 °C the bodies had a density exceeding 99%t.d. and grain size below 80 nm. The sintering activation energy of zirconia nanoceramics was more than twice lower than sintering activation energy of submicrometric zirconia.

## 1. INTRODUCTION

Ceramics of less than 100 nm in grain size is generally referred to as nanocrystalline ceramics or also nanoceramics. The reason why nanocrystalline ceramics are made and studied consists in their promising unique properties, based on the growing significance of grain boundaries [1,2]. The problems currently solved in the area of nanoceramic materials include not only the synthesis of powders but also their consolidation, shaping, and subsequent sintering [1].

The sintering of nanoparticle ceramics exhibits certain specific features. The best known and most frequently quoted are the low sintering temperatures of nanopowder compacts [3]. These are due to the high driving force of sintering when compared with conventional ceramic powders of coarser structure. Nanoparticle ceramic powder materials are also unique because of their low activation energy of sintering. For example, the activation energy of sur-

face diffusion of nanoparticle  $\text{Al}_2\text{O}_3$  is about  $230 \text{ kJ}\cdot\text{mol}^{-1}$  [1] while for conventional  $\text{Al}_2\text{O}_3$  it is usually given as about  $540 \text{ kJ}\cdot\text{mol}^{-1}$  [4] (values given by different authors can slightly differ).

Unfortunately, nanoceramic powders are usually not formed by isolated separate crystals; they contain agglomerates of primary particles. With increasing size of the agglomerates the size of the interagglomerate pores also increases. To make these big pores disappear, it is necessary to use higher sintering temperatures, which lead to increased grain boundary mobility and thus also to faster grain growth. If in the course of sintering the agglomerated material reaches a high density, it cannot be expected to have a resultant nanograined structure. Pressureless sintering cannot therefore yield final structures with grains smaller than the size of agglomerates contained in the microstructure of the initial green body [5].

Recently, we reported the results of cold isostatic pressing and pressureless sintering of zirconia

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nanopowders (stabilized with 1.5 and 3 mol.% of yttria) [6]. The bodies had final relative densities slightly above 90%t.d. and grain size about 80 nm after sintering at a temperature of 1100 °C. Pore size distribution in green bodies was found as the most important factor for sintering behaviour of the samples.

The aim of the present work was the preparation of bulk zirconia nanoceramics with high sintered density, and a comparison of sintering activation energy of nanometre-sized and submicrometre-sized powder compacts.

## 2. EXPERIMENTAL

For the preparation of powder compacts, the so-called green bodies, zirconia stabilized with 1.5 and 3 mol.% of yttria was used, which had been prepared by sol-gel synthesis from a solution of zirconium propoxide and yttrium nitrate in presence of ammonia. The product obtained was washed several times, first with distilled water and then with alcohol. After drying at 100 °C, the amorphous powder precipitate was changed to the crystalline phase via calcination in air atmosphere at 450 °C/5 h. According to yttria content, the powders were designated as Z-1.5Y and Z-3Y. In comparison with previously reported synthesis [6], the milling of the calcined powder was omitted. Milled powder [6] was designated Z-3Y-M in this paper.

For comparison, submicrometre-sized zirconia powder stabilized with 3 mol.% yttria, commercially available from Tosoh (Japan) and denoted TZ-3YB, was also used.

The particle size of ceramic powders was assessed by the BET method (ChemBET-3000, Quantachrome, USA). On the assumption of spherical shape and unimodal distribution of ceramic particles, the measured specific surface area (SSA) was converted to particle diameter ( $d_{\text{BET}}$ ). The list of

used ceramic materials including their particle size is given in Table 1.

Powder compacts were prepared by cold isostatic pressing (Autoclave Eng., USA) at a pressure of 300 MPa. The pore size distribution in green bodies was measured using a Pascal 440 (Porotec, Germany) mercury porosimeter.

The bodies were sintered in a high-temperature dilatometer (Linseis L75/50, Germany) at a heating rate of 5 °C/min up to a sintering temperature (1100 °C or 1500 °C). The holding time at the sintering temperature was 240 min. The dilatometer recorded the shrinkage values of bodies in dependence on temperature and time. Shrinkage values were converted to relative density subsequent to subtracting the thermal expansion of material as established from the cooling curves. Using Archimedes' principle the final density of sintered bodies was measured. The bodies were then cut, polished and thermally etched. The microstructure of thermally etched specimens was examined on an electron microscope (Philips XL30, the Netherlands) and the grain size was established via image analysis (Atlas software, Tescan, Czech Republic).

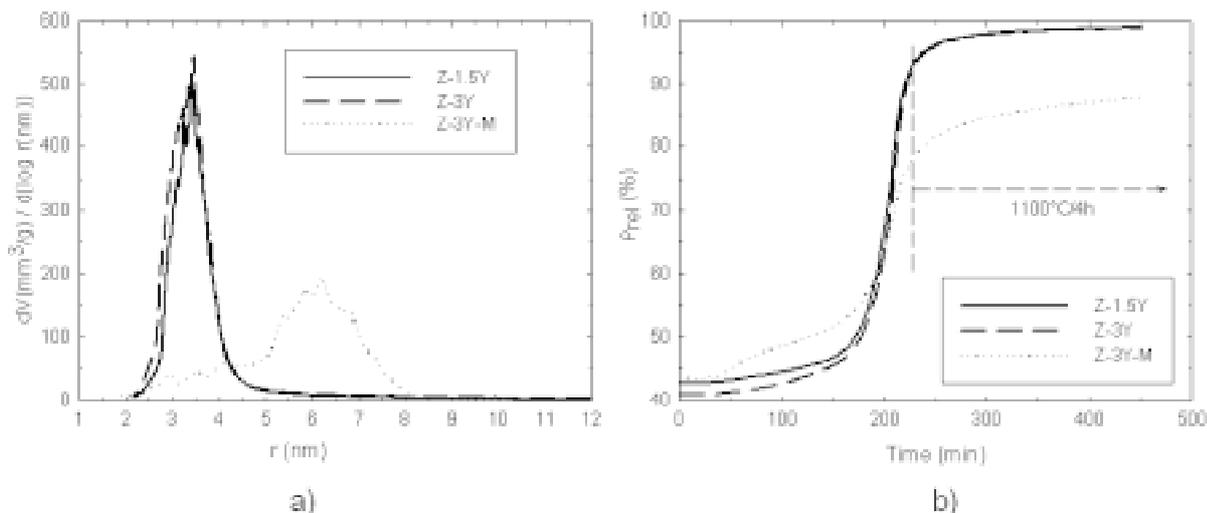
## 3. RESULTS AND DISCUSSION

As you can see from the Table 1, particles Z-1.5Y and Z-3Y had particle size less than 10 nm. Fig 1. shows the pore size distribution of the Z-1.5Y and Z-3Y green bodies prepared via cold isostatic pressing and its influence on sintering behaviour. For comparison, porosity and sintering kinetics of Z-3Y-M are included in the graphs.

Pore size distribution of all three samples was unimodal, most frequent pore radius of Z-1.5Y and Z-3Y samples was about 3.5 nm, sample Z-3Y-M (milled powder) had most frequent pore radius 6.2 nm [6]. More than 90% of pores had pore radius smaller than 5 nm in the case of Z-1.5Y and Z-3Y

**Table 1.** Specific surface area (SSA) and particle diameter ( $d_{\text{BET}}$ ) of zirconia powders, and relative density ( $\rho_r$ ) and grain size ( $D$ ) of sintered bodies.

Sample	Yttria content	SSA (m <sup>2</sup> /g)	$d_{\text{BET}}$ (nm)	Sintering (°C / h)	$\rho_r$ (%)	$D$ (nm)
Z-1.5Y	1.5 mol.%Y <sub>2</sub> O <sub>3</sub>	103	9.5	1100 / 4	99.0	79
Z-3Y	3 mol.%Y <sub>2</sub> O <sub>3</sub>	123	8.0	1100 / 4	98.9	66
Z-3Y-M	3 mol.%Y <sub>2</sub> O <sub>3</sub>	87	11.4	1100 / 4	87.8	80
TZ-3YB	3 mol.%Y <sub>2</sub> O <sub>3</sub>	6.5	152	1460 / 0	99.1	200



**Fig. 1.** Pore size distribution (a) and sintering kinetics (b) of nanometre-sized zirconia powder compacts pressed at 300 MPa.

samples, resp. smaller than 8 nm in the case of Z-3Y-M sample.

The smaller pore size resulted in better sintering behaviour – samples Z-1.5Y and Z-3Y reached final relative density about 99%t.d., whereas Z-3Y-M had the final density only 88%t.d. The yttria content did not significantly influence sintering behaviour of zirconia samples.

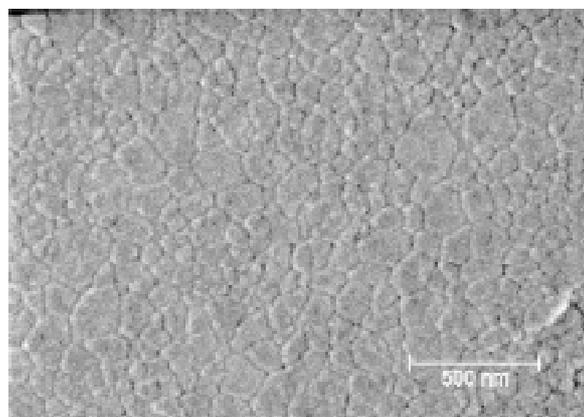
Fig. 2 shows the microstructure of Z-3Y sample. In accordance with the high value of final relative density there are only few pores visible in the microstructure. Average grain size was 66nm (Table 1), maximum grain size was 250nm.

Fig. 3a shows the difference in sintering kinetics for nanometre (Z-1.5Y and Z-3Y) and submicrometre (TZ-3YB) zirconia. The aim of the subsequent part of work was to find out whether these different-sintering samples are subject to identical sintering mechanisms expressed by theoretical models.

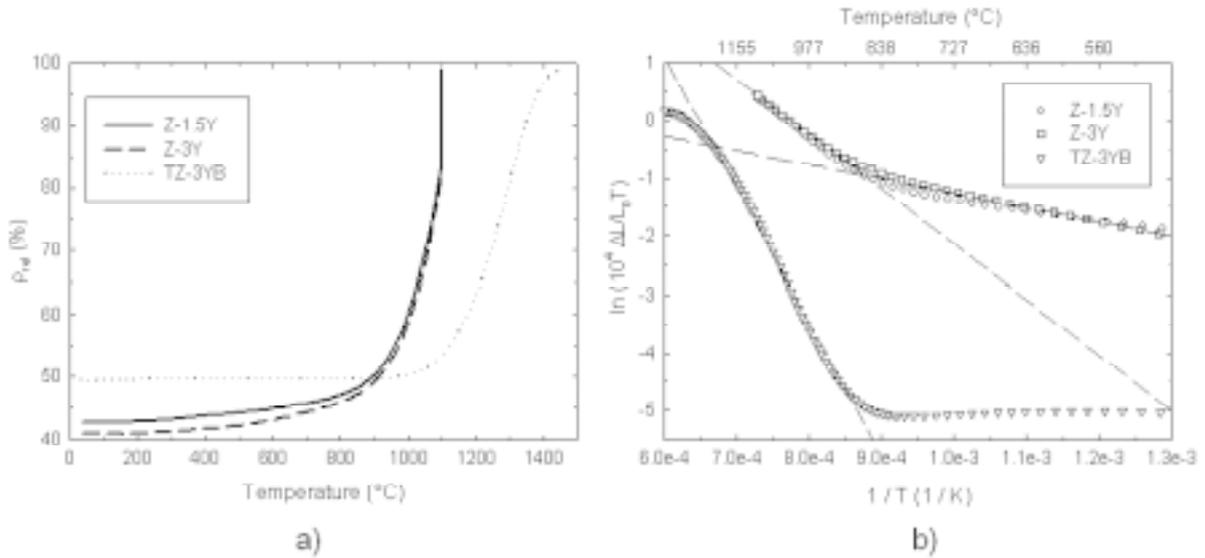
With the temperature increasing, the TZ-3YB sample did not change its density up to a temperature of ca 1000 °C, when necks began to be formed between particles (first sintering phase), growing successively and changing into the second sintering phase and third sintering phase. Comparing the first sintering phases of Z-1.5Y and Z-3Y and TZ-3YB, we can see that the initial sintering phase of nanoparticle  $\text{ZrO}_2$  is spread over a broad temperature zone (ca 250 – 930 °C) while the sintering kinetics curve of coarser TZ-3YB particles exhibits in

the first sintering phase of relatively sharp change in the line slope over a short temperature interval (1000 – 1150 °C).

The shrinkage of nanoparticle zirconia samples already at very low temperatures might be due to two effects. One possible reason is the change in length resulting from the desorption of gas and vapour molecules adsorbed on the surface of ceramic particles. If we consider adsorption of nitrogen with a molecule of 0.36 nm in size and if we assume the formation of monomolecular layer of  $\text{N}_2$  on the surface of ceramic particles of zirconia, then the shrinkage due to desorption would be 3.8% for nano-par-



**Fig. 2.** Microstructure of sintered Z-3Y sample.



**Fig. 3.** Sintering kinetics of nano- and submicrometric zirconia: a) densification, b) calculation of sintering activation energy.

ticle Z-3Y with particle size  $d = 8$  nm, and only 0.6% for TZ-3YB with particle size  $d = 62$  nm.

The other possible explanation for the shrinkage of nanomaterial at low temperatures is based on the hypothesis of the 'zero phase' of nanoceramic sintering. The high curvature of the surface area of nanometre particles leads to a high energy of the sintering process. Diffusion can therefore start taking place in nanoceramics at markedly lower temperatures that is the case of microparticle materials. It is at points of contact of crystallographically suitably oriented nanoparticles that formation of primary necks or particle sliding or mutual particle rotation may occur. Both above mentioned effects may result in increased relative density of nanoparticle samples already at relatively low temperatures.

For the description of sintering kinetics of the two samples in the area of open porosity the model by Young and Cutler [7] has been chosen, which starts from the kinetics principles formulated by Frenkel and Johnson. After simplification [8], the model chosen has the form:

$$\frac{\Delta L / L_0}{T} = \text{const} \cdot e^{-\frac{mQ}{RT}}, \quad (1)$$

where  $m$  is a constant which for the volume diffusion is 1/2 and for the grain boundary diffusion 1/3. Taking the logarithm yields:

$$\ln\left(\frac{\Delta L}{L_0 T}\right) = \ln(\text{const}) - \frac{mQ}{RT}. \quad (2)$$

It can be seen in Fig. 3b that in the open porosity area the dependence expressed by Eq. (2) is of straight-line nature, which means that sintering kinetics of the two materials is governed by diffusion and that one type of diffusion was predominant. It will be assumed that diffusion along grain boundaries was involved and so the constant  $m$  is 1/3. From the slope of fitted straight lines we can via comparison with (2) obtain the activation energy values:

$Q = 550$  kJ/mol for submicrometric  $\text{ZrO}_2$  (TZ-3YB) and

$Q = 237$  kJ/mol for nanometric  $\text{ZrO}_2$  (Z-1.5Y, Z-3Y).

Although the model given by Eq. (2) involves certain simplification, the activation energy values found can be taken for a qualified estimate that confirms the above literature data [1], namely that the activation energy of sintering of nanopowders is significantly lower than is the case with submicrometric ceramics.

The same as from Fig. 3a it is evident also from Fig. 3b that contrary to submicrometric ceramics the sintering of nanoparticle samples occurs already at low temperatures, which is probably due to the processes mentioned above. In view of the fact that the sintering kinetics of Z-15Y and Z-3Y material in the low-temperature region satisfied the linearity given by Eq. (2), it can be assumed that the processes that came to show in this region were also thermally activated. Their activation energy was more than 3 times less than the activation energy estab-

lished for this sample in the region of higher temperatures.

#### 4. CONCLUSION

Zirconia nanoparticles (stabilized by 1.5 and 3 mol.% of yttria) with particle size below 10 nm were prepared by sol-gel synthesis. Isostatically pressed green bodies had pore radii smaller than 5 nm. After pressureless sintering at 1100 °C the bodies had a density exceeding 99%t.d., and grain size below 80 nm. The value of sintering activation energy was established from sintering kinetics and it was 237 kJ·mol<sup>-1</sup> for zirconia nanoceramics. This value of activation energy is more than twice lower than sintering activation energy of submicrometric zirconia. The so-called 'zero sintering phase' was characteristic of the sintering of nanoparticle zirconia.

#### ACKNOWLEDGEMENTS

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