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Consolidation and sintering of nanometric ceramic powders

Ł. ZYCH*

AGH University of Science and Technology, Faculty of Materials Science and Ceramics,
al. Mickiewicza 30, 30-059 Cracow, Poland

Two powders containing 97 mol % ZrO_2 and 3 mol % Y_2O_3 with different crystallite sizes have been prepared by the hydrothermal method and calcination of co-precipitated gel. The hydrothermal powder was filter pressed under 5 MPa and dry pressed under 20 to 200 MPa. Filter pressed samples showed a more uniform particle arrangement than dry pressed samples which resulted in a better densification of the samples during sintering. Milling in water, and subsequent sedimentation of the calcinated powder allowed selecting fine particles for the filter pressing process.

Key words: *zirconia nanopowder; suspension; pressure filtration; sintering*

1. Introduction

Today many ceramic materials can be produced in a form of nanopowders with particle sizes below 100 nm. As a result of their activity related to a high surface area, they have recently been applied in many fields of technology such as cosmetic industry, catalysis, polymer processing etc. Sintering of ceramic nanopowders may lead to dense, nanocrystalline materials attractive due to their mechanical and electrical properties such as superelasticity at low temperatures, and high ionic conductivity. Nanopowders sinter at considerably lower temperatures than conventional powders, but their effective sintering, i.e. densification without extensive grain growth requires application of a consolidation technique which would lead to a uniform nanoparticle packing in a green body. Nanopowders tend to form agglomerates whose presence in the green body results in a wide pore size distribution. Based on the Kingery and Francois concept of the critical pore size [1], it is clear that small intra-agglomerate pores disappear during sintering process, while relatively large inter-agglomerate pores remain in a sintered body and hinder its densification.

*E-mail: lzych@agh.edu.pl

Uniform arrangement of particles during uniaxial pressing of nanopowders requires high pressures, often in the range of GPa [2, 3], which are necessary to crush agglomerates and overcome friction forces acting between nanoparticles. In the case of isostatic pressing, the applied pressures are lower, but still they are relatively high for this technique [4]. High compacting pressures cause many technological problems and generate internal stresses in a green sample, which may lead to sample cracking [2]. It seems that uniform particle arrangement in green samples can be achieved by means of one of the colloidal shaping techniques, e.g. centrifugal casting [5] or filter pressing [6]. A liquid wetting nanoparticles acts as a "lubricant", and allows them to move more easily and to arrange in a more uniform manner. Moreover, wet shaping techniques provide a better control of the shaping process than dry pressing [7].

The aim of this work was application of the filter pressing technique to consolidation of two zirconia nanopowders with different crystallite sizes, and investigation of their sintering process. Results of the filter pressing of the hydrothermal powder were compared with those of its dry unixial pressing.

2. Experimental

Two 3 mol % yttria-doped zirconia powders with different crystallite sizes were prepared by the co-precipitation method followed by hydrothermal treatment or calcination of X-ray amorphous gel. The common solution of $ZrOCl_3$ and YCl_3 was introduced into aqueous solution of ammonia. The co-precipitated gel was washed with distilled water in order to remove NH_4Cl. A part of the gel was hydrothermally treated at 250 ºC for 4 h under an autogenous water vapour pressure [8], and the other part was calcinated at 850 ºC for 1 h followed by attrition milling of the synthesised powder in ethanol for 5 h. The specific surface areas of the powders were measured by the BET method (Nova 1200e, Quantochrome Ins.). The crystallite size was determined by the X-ray diffraction method (CuK_α, X'Pert Pro, Philips) using the Scherrer formula, and the powders were observed under a TEM microscope (AEM CM 20, Philips). The average crystallite size of the hydrothermal powder was about 8 nm. The powder was kept in water suspension of the concentration of ca. 9 vol. %. Part of the suspension was dried at 120 ºC, and the resulting powder was ground below 5 μm and then uniaxially dry pressed under 20–200 MPa. The dry pressed samples were sintered at 1150 ºC for 2 h [9].

The original suspension of the hydrothermal powder was electrostatically dispersed by adjusting pH to 3 with HNO_3, and after 1 min of ultrasonification it was filter pressed in the apparatus shown in Fig. 1 [10]. The suspension was pressed with a steel piston (30 mm diameter) against a ceramic filter covered with a few layers of filter paper, and cellulose films. Pressure was increased up to 5 MPa, and kept constant until no water leakage was observed. Green samples were carefully dried up to

the constant weight at ambient temperature in a dessicator over silica gel. The green density of the samples was measured based on their weight and dimensions.

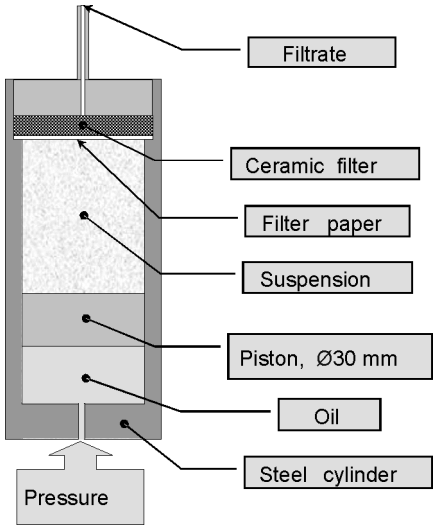

Fig. 1. Filter pressing apparatus

The average particle size of the calcinated powder was about 18 nm. The powder was milled for 24 h in water at pH 3, and after that it was left to sediment for 24 h, then the stable suspension collected from the sediment was filter pressed under 5 MPa. Particle sizes in both suspensions, as well as in the dried powders were determined using the DLS technique (Zetasizer Nano-ZS, Malvern Inc.). Before measurement, the dried powders were dispersed in water at pH 3, and all suspensions were ultrasonicated for 1 min.

The filter pressed samples were heat-treated at temperatures ranging from 600 ºC to 1400 ºC in air. Temperature was increased at the rate of 6 ºC/min to a predetermined level, and kept constant for 30 min, then the samples were cooled with a furnace. The apparent density of the sintered sample was measured by the Archimedes method, the pore size distribution was evaluated using mercury porosimetry (Poremaster 60, Quantachrome Ins.), and the microstructure was observed using a SEM microscope (Leo 1530). The theoretical density (TD) of 3 mol % Y–TZP used in calculations was 6.08 g/cm^3.

3. Results and discussion

3.1. Characteristics of powders

TEM microphotographs of the zirconia nanopowders are shown in Fig. 2, and their particle sizes determined by three different methods are given in Table 1. Particle sizes of the hydrothermal powder determined from TEM micrographs and calculated from X-ray diffraction line broadening are very close to that calculated from the pow-

der specific surface area, which indicates that no broad contacts between particles were formed. The value of the particle size of the calcinated powder calculated from the specific surface area was significantly higher than the other two values suggesting formation of phase contacts between particles during the calcination process.

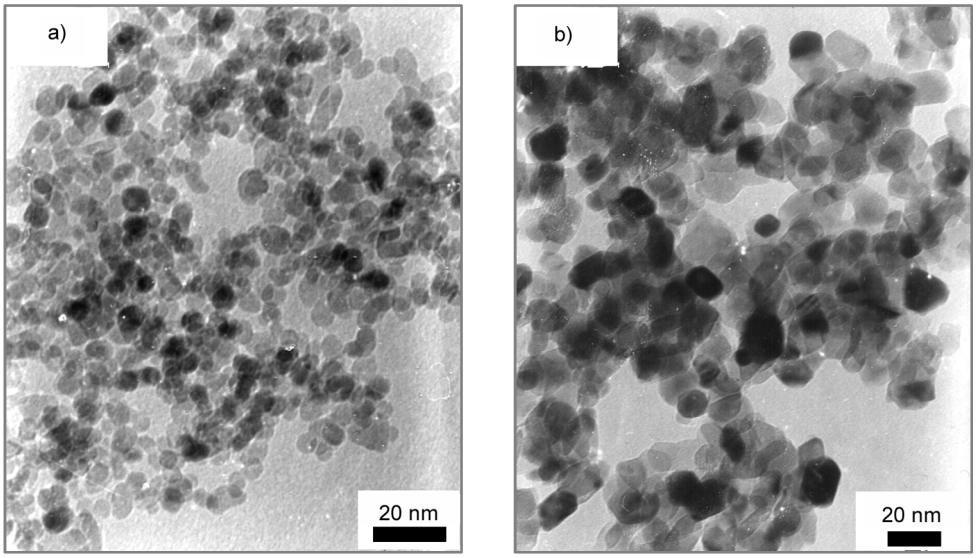

Fig. 2. TEM microphotographs of zirconia nanopowders: a) hydrothermal, b) calcinated

Table 1. Particle sizes of the zirconia nanopowders

Material	D_{BET} [nm]	D_{TEM} [nm]	D_{hkl} [nm]
Hydrothermal powder	8.1 ± 0.4	7.5 ± 0.2	8.6 ± 0.2
Calcinated powder	26.8 ± 1.3	17.9 ± 0.7	18.9 ± 0.2

Particle size distribution provides more useful information on the characteristics of powders than the calculated mean particle size (Fig. 3). The particle size distribution of the hydrothermal powder in the original suspension was relatively narrow with the modal value of about 47 nm, which means that no single crystallites were present in the suspension. Dried hydrothermal powder consisted of much larger particles, even of micrometric size. The original calcinated powder consisted mainly of submicron particles (modal values 177 nm and 530 nm). Milling of the calcinated powder for 24 h with a subsequent sedimentation shifted the particle size distribution towards smaller values (modal size 56 nm) but still some much larger particles remained in the powder.

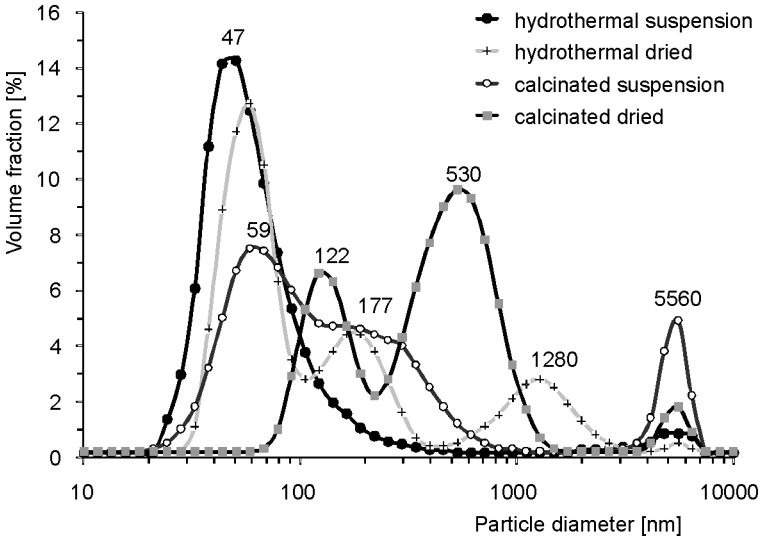

Fig. 3. Particle size distribution of hydrothermal and calcinated powder

3.2. Consolidation of the hydrothermal powder

The hydrothermal powder was consolidated by dry uniaxial pressing, and filter pressing of its water suspension (Fig. 4). The green density of dried, filter pressed samples did not depend on the applied filtration pressure. On the other hand, pressures higher than 5 MPa lead to cracking of samples during drying, thus this value was used in the powder consolidation. The relative density of the green filter pressed samples was about 40%, which is comparable with the density of samples dry pressed under 200 MPa (Fig. 4).

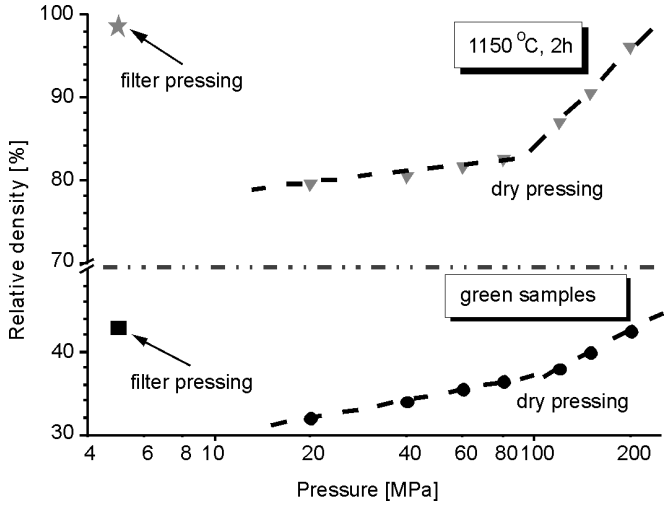

Fig. 4. Relative density of the samples prepared from the hydrothermal powder in function of compaction pressure

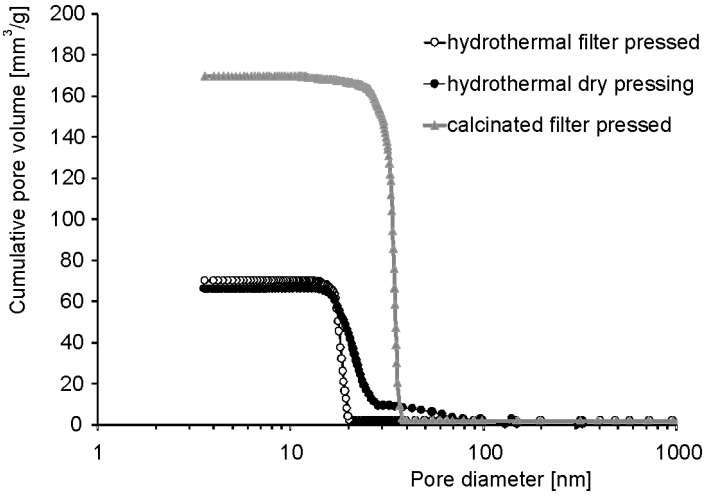

Fig. 5. Pore size distribution in dry pressed,
and filter pressed samples sintered at 1000 ºC, 1h

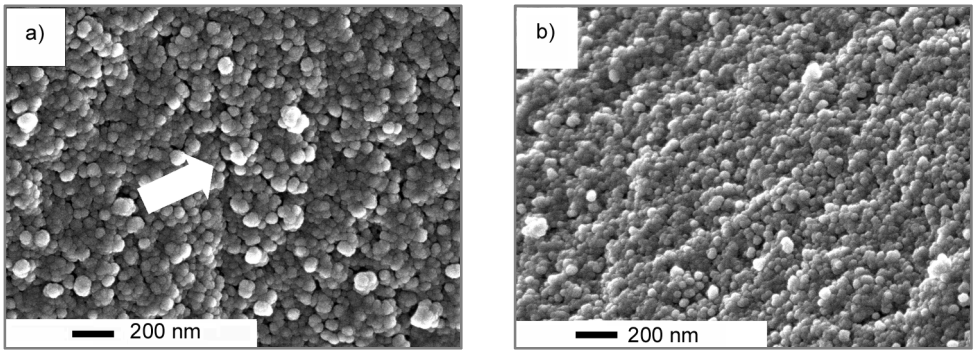

Fig. 6. SEM micrographs of green samples prepared by:
a) dry pressing, b) filter pressing of the hydrothermal powder

After sintering at 1150 ºC for 2h, the filter pressed sample densified to 98.5% TD, while the sample dry pressed under 200 MPa reached 96.0% TD. The differences in the sintering behaviour between the two samples can be related to non-uniform arrangement of the particles in the dry pressed sample resulting in a wide pore size distribution (Fig. 5). Larger pores are created between agglomerates which survived the compaction process (Fig. 6a). Such pores are detrimental to the sintering process, and cannot be removed under usual sintering conditions. Contrary to that, the pore size distribution of the filter pressed samples is extremely narrow, which means a uniform arrangement of the particles (Fig. 6b) and is beneficial for the sintering process. The filter pressed samples reached 99.99% TD after sintering at 1200 ºC for 30 min (Fig. 7), and grain size was in the range 100–200 nm (Fig. 8).

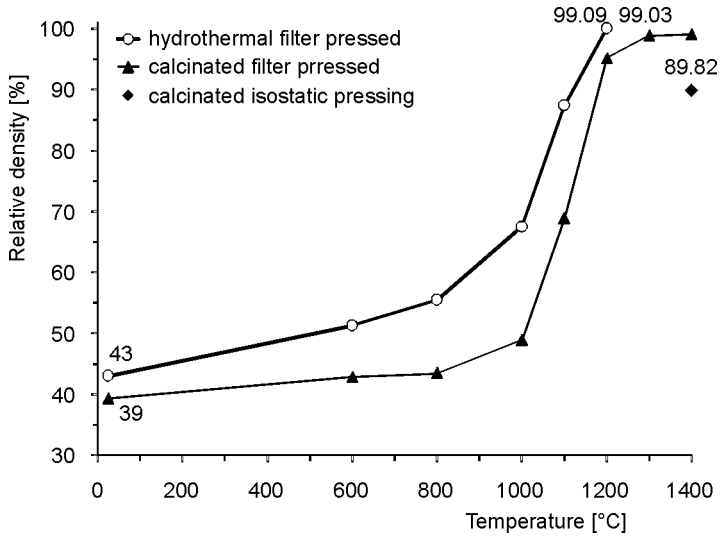

Fig. 7. Relative density of samples vs. sintering temperature (0.5 h, 6 ºC/min)

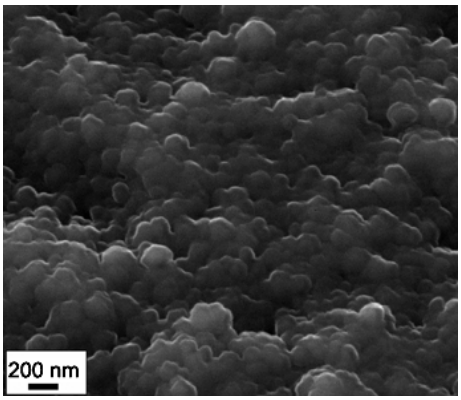

Fig. 8. SEM microphotograph of a fracture surface of the filter pressed sample sintered at 1200 ºC, 0.5 h

3.3. Consolidation of the calcinated powder

The main goal of the calcinated powder ball milling in a dispersing medium (water, pH 3) with subsequent sedimentation was to select possibly finest particles for the consolidation process (Fig. 3) which would lead to sample densification at a temperature lower than in the case of the original powder. Filter pressing of the milled powder lead to a green body of about 40% TD and a very narrow pore size distribution, similar to that of the hydrothermal powder but with a larger modal pore size (Fig. 5). The filter pressed samples reached 99.03% TD after sintering at 1400 ºC for 30 min, while samples consolidated by isostatic pressing of the original powder under 250 MPa achieved 89.82% TD (Fig. 7). This clearly results from the presence of large agglome-

ates (Fig. 3) in the original powder and a wide pore size distribution in the dry pressed samples (Fig. 5).

4. Summary

Filter pressing of zirconia nanopowder under 5 MPa led to a sample of about 40% theoretical density being similar to the density of a sample uniaxially pressed under 200 MPa. Filter pressed samples had very uniform particle arrangement which resulted in a better sintering behaviour. Samples prepared from the hydrothermal powder sintered at 1200 ºC for 0.5 h reached almost full density with the grain size of about 150–200 nm. Filter pressed samples of the calcinated powder reached 99.03% TD after sintering at 1400 ºC for 0.5 h.

The filter pressing method can be used for successful shaping of ceramic nanometric powders, although further studies are necessary to make use of its potential.

Acknowledgements

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