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Filter pressing and sintering of a zirconia nanopowder

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Abstract

The aim of this work was investigation of the sintering behavior of a material prepared by filter pressing of a zirconia powder with grain sizes of about 8 nm. The water suspension of the powder was filter pressed under 5 MPa. The observation of the microstructure evolution in samples heat-treated at different temperatures was performed. The crystallite arrangement in the material was very uniform, which led to uniform densification of the material. Heat treatment of the sample for 30 min at 1200 °C resulted in the material of 99.9% relative density, and grains not larger than 150 nm.

Keywords: Shaping; Sintering; Suspensions; ZrO_2; Nanopowder

1. Introduction

One of the group of materials which are still in the center of interest is nano-crystalline materials. Their properties, are inaccessible for coarse-grained polycrystals, e.g. superplasticity. Nano-crystalline materials are usually produced from powders with grain sizes below 20 nm, but such powders tend to form strong agglomerates. Although numerous methods of producing nanopowders were elaborated, serious processing problems are still encountered, mainly due to the friction between powder particles, which leads to non-uniform densification of the powder. The local differences in a green body density are related to the presence of pores of different size, and during sintering process finer pores disappear faster than the coarse ones. Removing of the later ones requires higher sintering temperatures, which subsequently leads to disadvantageous grain growth, and sometimes makes impossible to produce dense nanocrystalline material. Full densification at relatively low sintering temperature of the samples moulded by dry compaction is possible but needs the application of extremely high pressures, sometimes in order of GPa.[1] Such shaping conditions are difficult to apply in practice, and they restrict the size of produced artifacts.

The uniform packing of nanometric particles can by achieved using one of colloidal techniques e.g. filter pressing, or centrifugal casting.[2] In the presence of a liquid phase which wets the nanometric particles and penetrates between them, the particles move more easily, which leads to their more uniform arrangement.

The aim of the work was investigation of sintering process of samples prepared by means of pressure filtration of a solid solution nanometric powder containing 3 mol % Y_2O_3 and 97 mol % ZrO_2.

2. Experimental

The 3 mol % yttria-doped zirconia powder was prepared by the hydrothermal treatment of X-ray amorphous co-precipitated gel of a given composition. The processing route was as follow: the mutual solution of $ZrOCl_2$ and YCl_3 was introduced into vigorously agitated ammonia water solution. The co-precipitated gel was washed with water, and then hydro-thermally treated at 250 °C for 4 h under an autogenous water vapour pressure.[3] The specific surface area of the powder and partially sintered samples was measured using BET method (Sorpty 1750, Carlos Erba Ins.) and their phase composition, and crystallite size was investigated by X-ray diffraction method (Cu K_α, X'Pert Pro, Philips) using

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Scherrer formula, and the powder was observed under TEM microscope (AEM CM 20, Philips). The average particle size of the powder was about 8 nm. The powder was kept in a water suspension. The interrelation between zeta potential and pH of the suspension was investigated using Nanosizer-ZS apparatus (Malvern Inc.). The flocculated, and dispersed suspensions were consolidated using pressure filtration technique in apparatus shown in Fig. 3. The suspensions of about 5 vol.% concentration were forced by a steel piston of 30 mm diameter through a ceramic filter covered with filter paper. Pressure was increased up to 5 MPa, and kept constant until no water leakage was observed. The samples were carefully dried up to the constant weight in a desiccator over silica gel. The green density of the samples was estimated using GeoPyc 1360 apparatus (Micromeretics). The samples were non-isothermally sintered up to 1200 °C in dilatometer (with heating rate of 6 °C/min), and isothermally heat-treated at temperatures ranging from 100 to 1200 °C. Temperature was increased with 6 °C/min ratio to a predetermined level. Sample soaking time at each temperature was 30 min. The sample apparent density was measured by the Archimedes' method, pore size distribution was evaluated by the mercury porosimetry (Porosimeter 2000, Carlos Erba Ins.), and the microstructure was observed under TEM microscope. In order to compare filter pressing with dry compacting of the powder, part of the original suspension was dried at 120 °C, and the resulting powder was uniaxially compacted under pressures from 20 to 200 MPa. Filter-pressed, and dry-pressed samples were isothermally sintered under various conditions.

3. Results and discussion

3.1. Powder characteristics

Fig. 1 is a transmission electron micrograph of the powder and its properties are listed in Table 1. The powder consisted of almost fully tetragonal ZrO_2 solid solution.

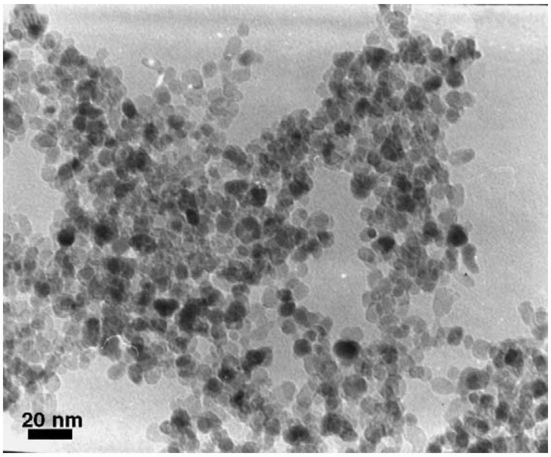

Fig. 1. Transmission electron micrograph of the 3 mol % Y_2O_3–ZrO_2 powder.

Table 1
Properties of the 3 mol % Y_2O_3–ZrO_2 powder

D_{BET} (nm)	D_{TEM} (nm)	$D_{(111)}$ (nm)
8.1	7.5	8.6

D_{BET}: particle size calculated on the basis of specific surface area determined by nitrogen adsorption. D_{TEM}: particle size observed under transmission electron microscope, D_{111}: crystallite size calculated on the basis of the X-ray diffraction method from tetragonal phase line (1 1 1) broadening.

The coincidence of the particle sizes determined by the three different methods indicates that particles are separated from each other; no crystallite boundaries form under the applied hydrothermal treatment conditions.

The powder was kept in a water suspension, which prevented formation of strong bonds between particles.

3.2. Shaping process

Fig. 2 shows the interrelation between zeta potential and pH of the suspension. The isoeletric point was located near pH 7, which was the original pH of the suspension. It means that the powder suspension was flocculated. According to the zeta-potential relation vs. pH the dispersed suspension was prepared by changing pH to 2 with HCl acid addition. The original (flocculated), and dispersed suspensions were filter pressed under 5 MPa (Fig. 3). Selection of this pressure value was based upon our previous investigations, which showed that the pressures from 2 to 20 MPa did not influence the sample green density. But samples formed under higher pressures tended to crack during drying. Green density of the samples was about 40% T.D. (T.D. = theoretical density, 6.02 g/cm^3).

Two layers differing in translucency occurred in samples filter pressed from dispersed suspension. This effect most probably is related to different densification of the layers, and not to the particle size segregation eventually due to sedimentation. The crystallite sizes of the two layers, as measured by the X-ray line broadening, were identical.

The two layers were separated with a sharp blade and sintered at temperatures ranging from 1000 to 1150 °C for 30 min. Fig. 4 shows relative density of the two layers vs. sintering temperature. It is evident that the layer adjacent to the

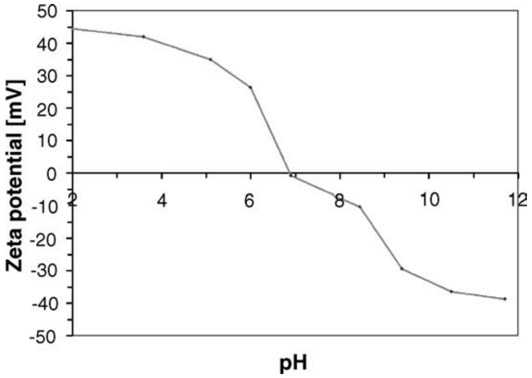

Fig. 2. Zeta potential vs. pH of the suspension.

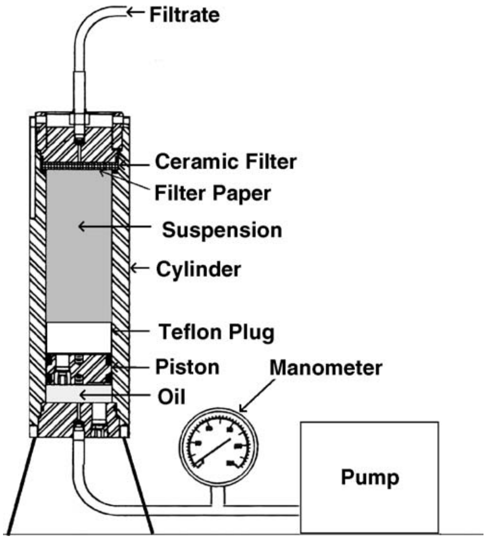

Fig. 3. Schematic drawing of the pressure filtration apparatus.

filter paper densifies better than the opposite one, most probably due to the higher green density of the former one. Contrary to de-flocculated suspension, the flocculated one resulted in uniformly densified samples. But its sintered density is slightly lower than the density of the both layers mentioned above (see Fig. 4). Plausible reason of the described phenomena should be attributed to the differences in the particle arrangement originating from the state of agglomeration of these suspensions.

Nevertheless, sintering behaviour was studied using the uniformly densified samples manufactured from the flocculated suspension.

3.3. Sintering

Curves in Fig. 5 show linear shrinkage of the samples during sintering in dilatometer with heating rate of 6 °C/min. The same plot presents also sintering curve of sub-micron commercial powder (Tosoh. Co.) with the same composition as the hydrothermally prepared powder. The sub-micron powder was uniaxially compacted under pressure which assured the same density of the starting samples as the green density of the filter pressed body.

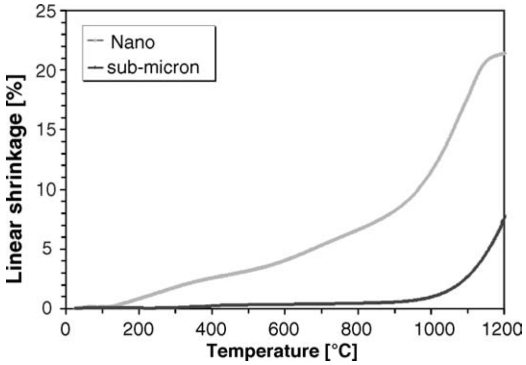

Fig. 5. Linear shrinkage of samples during non-isothermal sintering with the heating rate of 6 °C/min.

The sintering curves of both powders show distinct differences. Shrinkage of filter pressed samples starts at temperature as low as 200 °C, up to this temperature the sample expands. Thermal expansion coefficient calculated on this basis from room temperature up to 150 °C equals $0.89 \times 10^{-5}\,\mathrm{K}^{-1}$ and is close to the characteristic value of zirconia solid solutions. Specific surface area starts to decrease, beginning from temperatures higher than 350 °C (Fig. 6). It means that at these temperatures inter-crystalline boundaries begin to form. Infra-red spectroscopy indicated presence of free water most probably filling capillary volume and adsorbed on the high surface area ($130\,\mathrm{m}^2/\mathrm{g}$) of the powder. This is a plausible reason of the observed weight loss (Fig. 7).

Most probably capillary water evaporates from the system heat treated up to 150°, but adsorbed water still remains in the system. Thus, shrinkage of the system in the temperature range from 150 to 300 °C should be attributed to the evaporation of the adsorbed water layers. On the basis of the specific surface area of the powder and the fraction of adsorbed water (2.52 wt.%) we can assess the thickness of the water layer adsorbed on the powder surface. Its value of 0.2 nm is comparable to the size of the water molecule. The number of such layers along the unit length depends on the crystallite size and

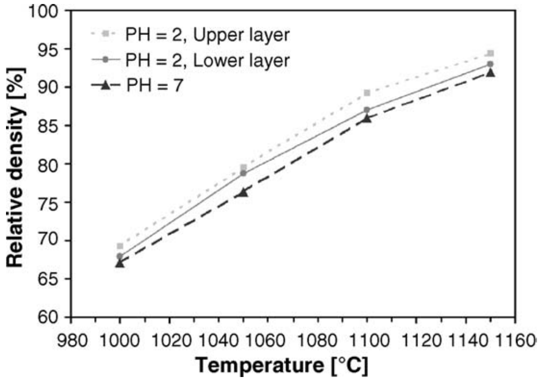

Fig. 4. Relative density of the layers vs. sintering temperature.

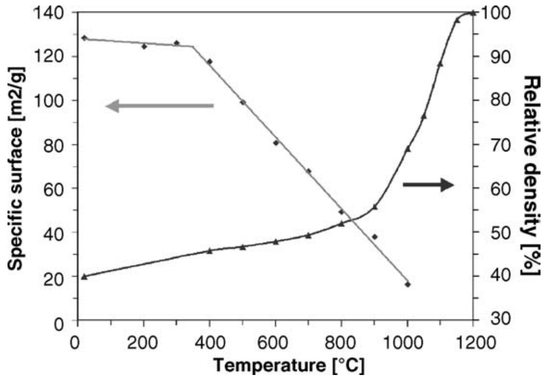

Fig. 6. Specific surface area, and relative density vs. temperature.

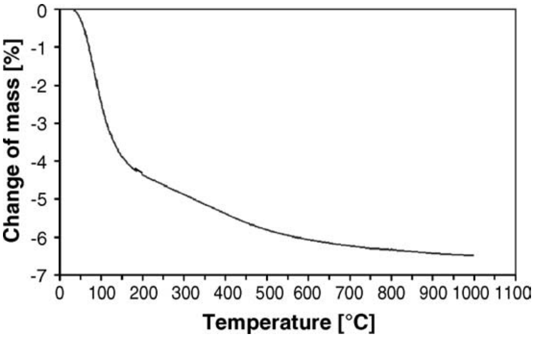

Fig. 7. Change of mass of filter pressed sample vs. temperature. Rate of temperature increase 10 °C/min.

packing density of the system. It allows us to estimate shrinkage due to desorption of water layers. It equals to about 1%, what corresponds to temperature of 350 °C during dynamic heating. Approximately at this temperature inter-crystalline grain boundaries start to form.

Shrinkage of the sub-micron powder starts at about 1000 °C, and at 1200 °C it reaches only 8%, what corresponds to about 60% T.D., while at this temperature the nanopowder shrinkage terminates, and the sample density is about 99% T.D.

Fig. 6 presents density of samples heated up to pre-selected temperatures in the range 100–1200 °C. Soaking time in each case was 30 min. Sample heat-treated at 1200 °C reached 99.9% T.D.

In order to compare filter pressing with dry compacting of the nanometric powder, part of the original suspension was dried, and the resulting powder was uniaxially compacted under 200 MPa. Fig. 8 presents pore size distribution curves of the dry-pressed and filter-pressed samples. Bimodal pore size distribution is evident in case of the dry pressed sample. Larger pores correspond to inter-agglomerate porosity and the smaller ones to the intra-agglomerate pore volume. The filter-pressed body shows mono-modal pore size distribution. It indicates more uniform particle arrangement in the latter case and non-uniform in the dry-pressed material.

These microstructural differences result in higher sintered density of the filter-pressed material compared to the dry-pressed one (Table 2).

It is interesting to notice, that in case of the dry-pressed material, open porosity exists in the material of 97% T.D., which is quite unusual behaviour. Such a situation does not exist in the filter-pressed samples.[4]

Table 3 presents modal pore size changes during sintering of the filter pressed samples. The same samples were used to assess crystallite sizes by the X-ray line broadening (Table 3). We observed simultaneous pore sizes and crystallite increase. This phenomenon usually accompanies densification and can be attributed to two factors.[5] One is related to the occurrence in the green body areas differing in packing density. The denser areas originate from the powder agglomerates which survive the shaping process. Within these areas porosity disappears faster than in the areas of lower density, causing essential increase of the pore sizes in the latter ones. Under usually applied sintering conditions such pores do not disappear. Another reason of pore growth results from the grain (crystallite) growth. Pores move with the grain boundaries

Table 2
Densification of samples sintered at 1150 °C for 2 h

Sample	Relative density (%)	Open porosity (%)
Dry-pressed	97.0	2.9
Filter-pressed	99.0	0

Rate of temp. increase 6 °C/min.

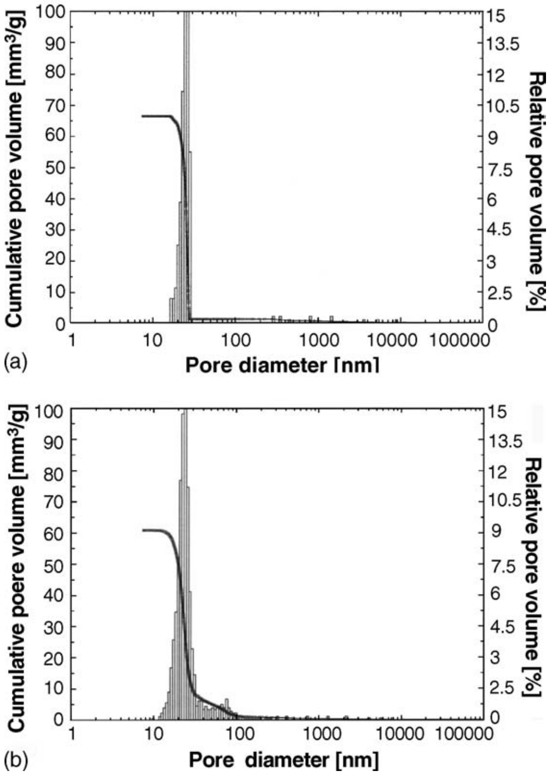

Fig. 8. (a) Pore size distribution in the filter-pressed sample heat treated at 1000 °C for 1 h. (b) Pore size distribution in the dry-pressed sample heat treated at 1000 °C for 1 h.

Table 3
Modal pore diameter, and crystallite size in samples heat treated at different temperatures

Temperature (°C)	Modal pore diameter taken from pore size distribution curves (nm)	Crystallite size calculated on basis of X-ray diffraction method (nm)
20	9.4	8.6
200	10.1	9.0
400	11.4	9.3
600	11.9	10.3
800	15.0	12.0
900	16.9	15.3
1000	20.8	20.1

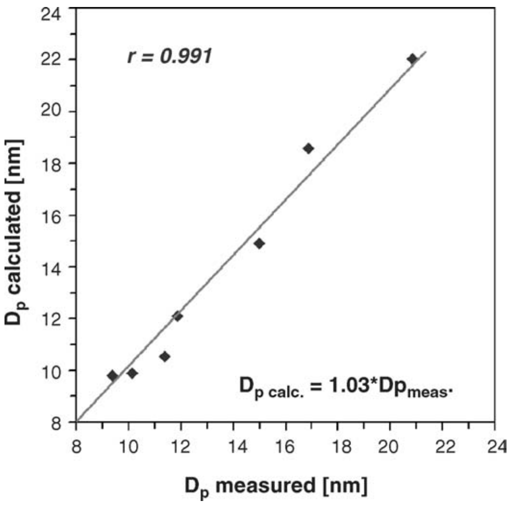

Fig. 9. Interrelation between measured, and calculated (Eq. (1)) pore size. (confidence level of regression = 99.9%).

under conditions of continuous grain growth. Coalescence of such pores is recorded as a pore size increase. If the latter of these two processes is dominating pore sizes measured and calculated, using a simple geometric relation, should agree:

$$\frac{D_{\mathrm{P}}}{D_{\mathrm{g}}} = \sqrt[3]{\frac{V_{\mathrm{P}}}{V_{\mathrm{g}}}}, \tag{1}$$

where D_{P} is pore size (modal pore size, Table 3); D_{g} is grain size (crystallite size, Table 3), V_{P} is volume fraction of pores, and V_{g} is volume fraction grains, respectively. V_{g} equals to relative density of the material (Fig. 6), and $V_{\mathrm{P}} = 1 - V_{\mathrm{g}}$.

Fig. 9 illustrates the interrelation between measured, and calculated pore sizes according to Eq. (1). Good correlation between measured and calculated pore sizes, indicates that they are equal to each other. It points out that pore growth can be ascribed to the growth of crystallites and not to the behaviour of the agglomerated system. Thus the crystallite arrangement in the filter pressed sample is very uniform. It leads to uniform densification of the material within its whole volume.

Another phenomenon related to the grain growth is the phase composition change in samples heat treated at different temperatures (Fig. 10). The green sample is almost fully tetragonal. However, with temperature the monoclinic phase amount increases, and reaches its maximum (18%) at 900 °C. Increase of the monoclinic phase quantity with temperature can be related to the fact, that some of the crystallites exceed critical size above which the tetragonal to monoclinic phase transformation occurs. As densification proceeds the system becomes more rigid. It impedes tetragonal to monoclinic transformation. Hence, monoclinic phase fraction decreases with sample densification during sintering.

Microstructure of sample sintered at 1200 °C for 0.5 h is presented in Fig. 11. The modal grain size estimated on the basis of several micrographs like this in Fig. 11 is about 100 nm.

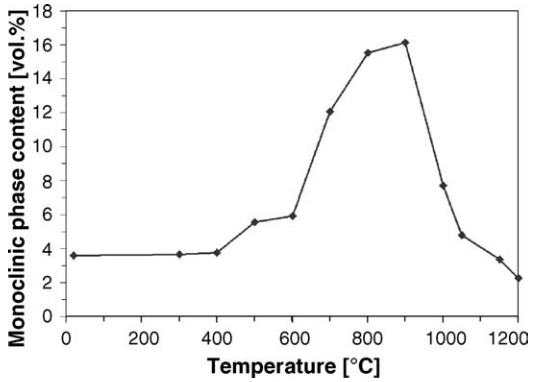

Fig. 10. ZrO_2 monoclinic phase amount vs. temperature.

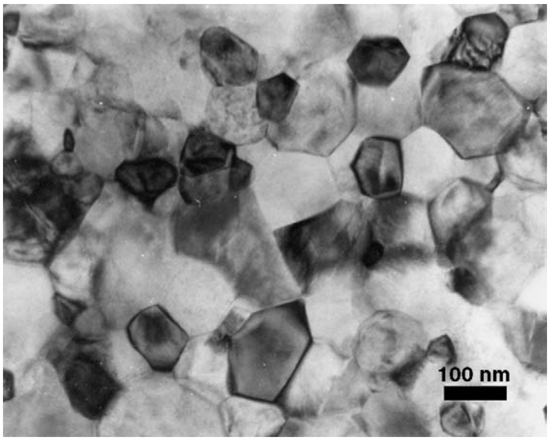

Fig. 11. Transmission electron micrograph of the sample sintered at 1200 °C for 0.5 h.

4. Summary

Application of the filter pressing method for the shaping of water suspension of nanometric (mean particle size 8 nm) zirconia powder resulted in green samples with homogenous particle arrangement and very narrow pore size distribution. Its sintering at 1200 °C for 0.5 h led to obtaining of dense material (99.9% T.D.) with modal grain size about 100 nm. Samples prepared from the same powder, but using dry uniaxial pressing had broader pore size distribution, which resulted in their lower densification than filter pressed samples under a given sintering conditions.

Acknowledgements

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