Rev.Adv.Mater.Sci. 5 (2003) 183-186

SINTERING OF BULK ZIRCONIA NANOCERAMICS

K. Maca, M. Trunec, P. Dobsak and J. Svejcar

Brno University of Technology, Technicka 2, 616 69 Brno, Czech Republic

Received: June 11, 2003

Abstract. The sintering and the microstructure of zirconia ceramics prepared by cold isostatic pressing of nanoceramic powders were studied. Ceramic powders contained 0, 1.5 and 3 mol.% of yttria. It was found that higher compacting pressures (700 MPa) yielded green bodies with smaller pores, which showed in their better sinterability. After sintering at 1100 °C, the bodies had a density exceeding 90% t.d. and grains below 80 nm. A critical ratio of the pore size in green bodies to the particle size was established, which enables sintering zirconia nanopowders of some 10 nm in size at a temperature of 1100 °C.

1. INTRODUCTION

Nanocrystalline ceramics represent a much promising material not only for structural but also for other applications, e.g. in optics, electronics and medicine [1]. The main limitation to evaluation of the unique properties of bulk ceramics and their exploitation in applications is the difficulty encountered when compacting agglomerated nanometric ceramic particles into an appropriate green body [1]. The structure of such nanoparticle green body (characterized by the particle size and the pore size distribution) must provide for sintering into dense nanoceramics with grains below 100 μm. The compacting of agglomerated nanometric particles can be improved by pressure sintering [2]. In view of the shape limitations of parts prepared in this way, and the high costs, pressureless sintering represents a more promising variant.

The aim of the present work is to assess the effect of compacting pressure in cold isostatic pressing of zirconia powders stabilized by different amounts of yttria on the microstructure of their green body, and to describe the effect of green body microstructure on the kinetics of sintering and on the final microstructure of sintered bodies.

2. EXPERIMENTAL

Three kinds of ceramic nanopowder were used in the preparation of ceramic green bodies, in the following referred to by these abbreviations:
Z0Y – pure non-stabilized zirconia (Nanostructured & Amorphous Materials, USA);
Z1.5Y – zirconia stabilized with 1.5 mol% of yttria;
Z3Y- zirconia stabilized with 3 mol% of yttria.

Stabilized Z1.5Y and Z3Y powders were prepared by precipitation synthesis from zirconium n-propoxide ($Zr(OC_3H_7)_4$) and yttrium nitrate ($Y(NO_3)_3$). A acidified solution of $Zr(OC_3H_7)_4$ and $Y(NO_3)_3$ in i-propanol was added by drops into the reactor with a water solution of ammonia under constant stirring. After precipitation the product was stirred intensively for 1.5 h. The precipitate was separated by centrifugation and washed with distilled water until pH was neutral. Water was removed from the product via i-propanol washing. The washed precipitate was dried at 250 °C and the powder was calcinated at 450 °C and then milled for 24 h.

For comparison, submicrometric zirconia stabilized with 3 mol% yttria, commercially available from Tosoh (Japan) and denoted TZ3Y-SE, was also used.

The size of ceramic powders was assessed by the BET method (Quantachrome, USA) and their

Corresponding author: K.Maca, e-mail: maca@umi.fme.vutbr.cz

Table 1. Selected properties of ceramic powders, green bodies and sintered bodies.

Material	*Compacting pressure* (MPa)	*D* (nm)	MFPR (nm)	HPR (nm)	*R*1= MPR/*D*	*R*2= HPR/D	*Final density* (%t.d.)	*Open porosity* (%t.d.)	*Closed porosity* (%t.d.)
Z0Y	300	11.8	4.2	19.4	0.35	1.64	87.8	11.2	1.1
Z0Y	700	11.8	2.9	5.5	0.25	0.47	91	0.6	8.4
Z1.5Y	300	11.8	4.9	9.1	0.42	0.77	84.5	10.8	4.7
Z1.5Y	700	11.8	2.4	3.6	0.20	0.31	92.3	0.2	7.5
Z3Y	300	11.4	6.2	11.8	0.54	1.04	87.8	7.6	4.6
Z3Y	700	11.4	3.0	6.3	0.26	0.55	91.1	0.1	8.8
TZ3Y-SE	300	152	19.2	26.3	0.13	0.17			

phase composition by X-ray diffraction (X'pert, Philips, the Netherlands). Specimens were moulded into disks (dia 25 mm, height 4 mm) by cold isostatic pressing (Autoclave Eng., USA) at a pressure of 300 MPa. Some of the specimens were subsequently isostatically pressed at a pressure of 700 MPa. The pore size distribution in pressed 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 of 1100 °C, at which temperature there was a holding time of 240 min. Using Archimedes' principle the final density of sintered bodies was measured. The bodies were then cut, polished and thermally etched (1100 °C/5min). 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

By gas adsorption measurement, the specific surface of ceramic powders was 87.8 m^2/g (Z0Y), 83.3 m^2/g (Z1.5Y) and 86.7 m^2/g (Z3Y). On the assumption of spherical shape and unimodal distribution of ceramic particles, the specific surface is easy to convert to particle size. The size of particles, expressed by their diameter *D*, was found to be 11.3 nm (Z0Y), 11.8 nm (Z1.5Y) and 11.4 nm (Z3Y), hence the powders in question were nanopowders. The TZ3Y-SE powder had a specific surface of 6.5 m^2/g and the particle size calculated from this specific surface is 150 nm (see Table 1).

The microstructure of ceramic green bodies was evaluated by mercury porosimetry. The plot of pore size distribution is given in Fig. 1. Table 1 gives the values of pore radii with maximum occurrence (most frequent pore radius = MFPR) and the values of maximum pore radii present in the green bodies (highest pore radius = HPR). It is clear from the Fig. 1 and from the Table 1 that all the samples had unimodal pore distribution and that higher compacting pressures resulted in reduced pore size. Similarly Gao *et al.* [3] found the decrease of average pore diameter in zirconia green bodies from 5.3 nm to 3.7 nm when they increased the compaction pressure from 450 MPa to 3GPa.

The sintering of bodies took place in the dilatometer, which 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. The plot of the dependence of relative density on time and compacting pressure is shown in Fig. 2. Table 1 gives the final densities of sintered bodies inclusive of the share of open and closed pores. In spite of the differences in the final density of specimens pressed under different pressures being not very great (in particular in the Z0Y and Z3Y specimens) the specimens pressed at a pressure of 300 MPa exhibited open porosity in contrast to those pressed at 700 MPa. This was also evident in the microphotographs: in contrast to the specimens pressed

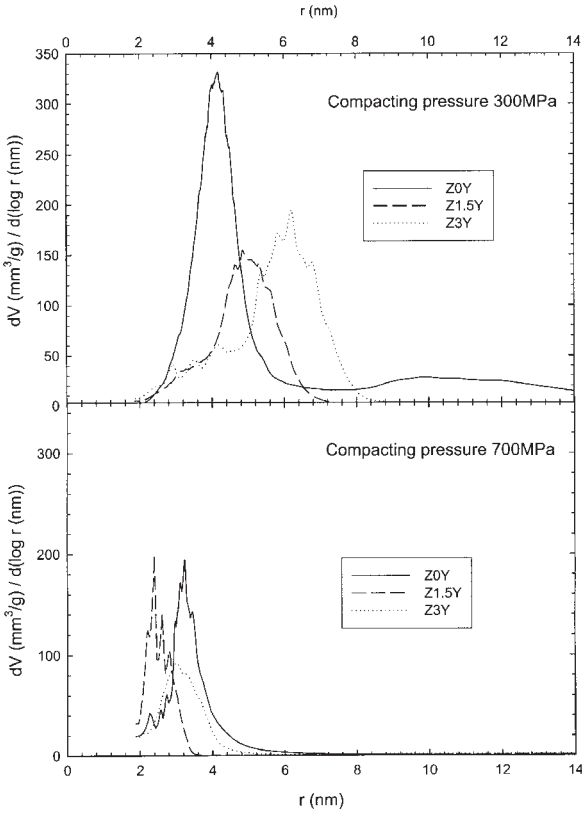

Fig. 1. Pore size distribution of zirconia green bodies.

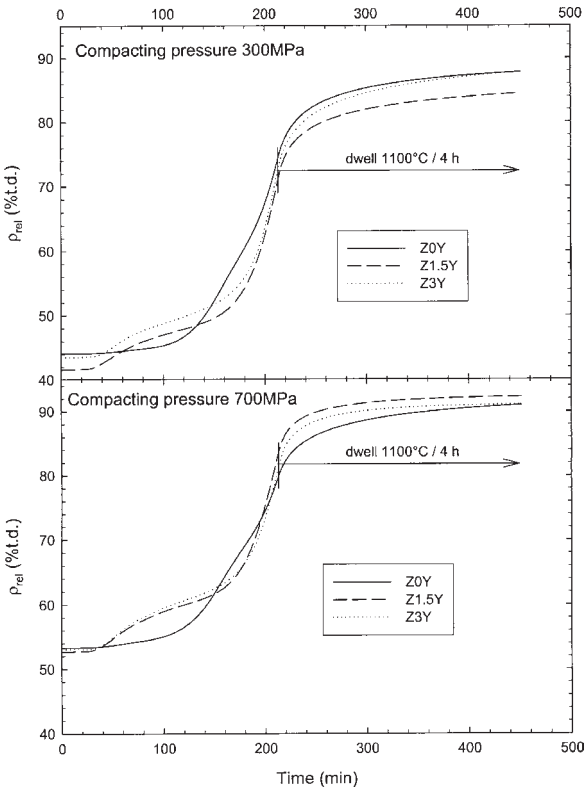

Fig. 2. Sintering kinetics of zirconia bodies.

under lower pressures the specimens pressed under higher pressures had a homogeneous structure and were without shrinkage porosity (see Fig. 3). The grain size ranged between 60 and 80 nm. The yttria content did not significantly influence sintering behaviour of zirconia samples.

The above results illustrate clearly the effect of the microstructure of green bodies on the sinterability of nanoceramics. The microstructure of bodies can be represented quantitatively using the ratios

$$R1 = \mathrm{MFPR} / D \qquad (1)$$

or

$$R2 = \mathrm{HPR} / D. \qquad (2)$$

Table 1 gives the values of $R1$ and $R2$. It is evident that decreasing values of these ratios are favourable for the sintering kinetics of nanoceramic particles. To sinter ceramic particles of ca 10 nm in size at a temperature of 1100 °C it is necessary for $R1$ resp. $R2$ to be less than 0.3 resp. 0.55. Bodies prepared from the TZ3Y-SE submicrometric powder exhibited the best (this means the lowest) $R1$ and $R2$ values despite having been pressed at a pressure of 300 MPa. This shows that with decreasing particle size the difficulty of compacting them increases. The low values of $R1$ and $R2$ themselves do not, of course, mean a low sintering temperature, the latter being naturally also a function of particle size [4,5], therefore TY3Z-SE sintered at temperatures

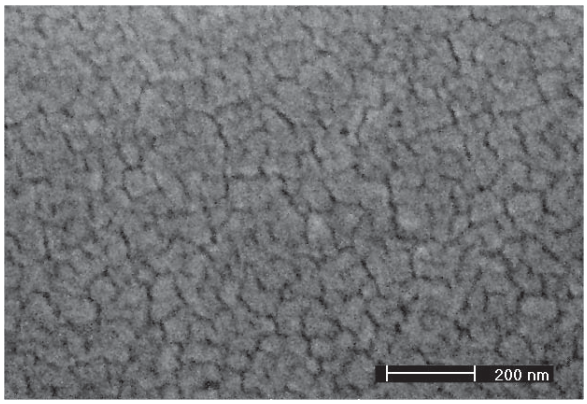

Fig. 3. The microstructure of sintered Z1.5Y specimen (compaction pressure 700MPa, sintering 1100 °C/4h).

higher than 1100 °C [6]. However, the $R1$ and $R2$ values can serve to classify green bodies prepared by different moulding methods from powders of the same or similar particle size. The lower the values of $R1$ and $R2$, the more homogeneous the microstructure of green body and the better the sinterability of the body.

4. CONCLUSION

Using the method of cold isostatic pressing, specimens with single-mode pore size distribution were prepared from three types of zirconia powder with a particle size of ca 10 nm. Applying high compacting pressure (700 MPa) led to reduced pores in the body so that these bodies could be sintered at a temperature of 1100 °C into a structure without open porosity (r_{rel} > 90 % t.d.) and with grains below 80 nm. A ratio of pore size and particle size was established that enabled sintering zirconia at a temperature of 1100 °C.

REFERENCES

[1] M. J. Mayo // *Int. Mater. Rev.* **41** (1996) 85.
[2] J. R. Groza and R. J. Dowding // *Nanostructured Mater.* **7** (1996) 749.
[3] L. Gao, W. Li, H. Z. Wang, J. X. Zhou, Z. J. Chao and Q. Z. Zai //*J. Eur. Ceram. Soc.* **21** (2001) 135.
[4] C. Herring // *J. Appl. Phys.* **21** (1950) 301.
[5] W. Zheng, L. Gao, L. Gui and J. Guo // *Ceram. Int.* **25** (1999) 723.
[6] K. Maca, H. Hadraba and J. Cihlar // *Ceramics-Silikaty* **42** (1998) 151.