Available online at www.sciencedirect.com
ScienceDirect
Scripta Materialia 59 (2008) 23–26
Scripta MATERIALIA
www.elsevier.com/locate/scriptamat

Warm pressing of zirconia nanoparticles by the spark plasma sintering technique

Martin Trunec,[a,*] Karel Maca[a] and Zhijian Shen[b]

[a]*Department of Ceramics and Polymers, Brno University of Technology, 616 69 Brno, Czech Republic*
[b]*Department of Inorganic Chemistry, Arrhenius Laboratory, Stockholm University, S-10691 Stockholm, Sweden*

Received 21 January 2008; accepted 15 February 2008
Available online 23 February 2008

Zirconia nanoparticles were densified by pressureless sintering and spark plasma sintering (SPS). The evolution of relative density and pore size distribution in powder compacts during these sintering processes were compared. It was found that pore size increase was suppressed during SPS and that this facilitated the densification. The combined sintering process (low-temperature pre-sintering by SPS followed by pressureless sintering) was performed to confirm the advantage of the low-temperature SPS technique (referred to as SPS warm pressing).

Keywords: Nanocrystalline materials; Powder processing; Pore structure; Grain growth; Sintering

Recently, much effort has been focused on the synthesis and densification of ceramic nanoparticles. The reason for the interest in nanocrystalline ceramics lies in their unique properties resulting from the small grain size, and the growing significance of grain boundaries in the nanocrystalline structure [1]. Nanocrystalline tetragonal zirconia represents a candidate material for a multitude of applications, including load-bearing structural applications, solid oxide fuel cells and bioceramic implants. Unfortunately, pressureless sintering of zirconia nanoparticles into bulk dense nanocrystalline bodies requires a specific green-body microstructure [2] that cannot easily be obtained. Pressure-assisted sintering techniques (hot pressing, sinter forging, hot isostatic pressing, spark plasma sintering, etc.) represent an alternative approach to the densification of nanoparticles.

Spark plasma sintering (SPS) is a promising method for the rapid densification of ceramic nanopowders at relatively low-temperatures. The high densification rate makes it a suitable means of preparing bulk nanostructured ceramics. The mechanisms responsible for high-rate densification were identified as grain rotation and sliding, aided by partial melting of the particle surface or plastic deformation in materials with low yield stress [3,4]. The pore size evolution in powder compacts could help to elucidate these processes, but no reports of this have been published. Densification due to normal grain growth takes place in SPS at higher relative densities (>85–90% theoretical density (t.d.)), regardless of the material [3,4]. The grain growth progresses very quickly in the last spark plasma sintering stage [5,6]. This suggests that the mass transport processes involved in the SPS are significantly enhanced. Moreover, the effects of heating rate and sintering time on densification and grain growth seem to be not fully understood because contradictory results have been reported by various authors [7]. These are probably the reasons why fully dense ceramics with nanocrystalline structure prepared by SPS have been reported only sporadically [8,9].

The objective of the present investigation was to describe the evolution of the pore size and density of nanopowder zirconia compacts during SPS and compare this behaviour to behaviour of compacts sintered without pressure. Combined densification by SPS with subsequent pressureless sintering was proposed to highlight the advantage of low-temperature SPS process (referred to as SPS warm pressing).

Tetragonal zirconia nanopowder stabilized with 1.5 mol.% Y_2O_3 (1.5 YSZ) was prepared by sol–gel synthesis [2]. The powder had a specific surface area (SSA) of 79 $m^2 g^{-1}$. The particle size calculated from the SSA was 12 nm and this size corresponded well to the particle size determined from TEM images.

* Corresponding author. Tel.: +420 541143339; fax: +420 541143202; e-mail: trunec@fme.vutbr.cz

1359-6462/$ - see front matter © 2008 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.scriptamat.2008.02.015

For pressureless sintering, the powder was compacted by cold isostatic pressing (CIP) at 300 MPa (disc with a diameter of 20 mm and a thickness of 5 mm). The nanopowder compacts were partially sintered without pressure (using a heating rate of 5 °C min^{-1}) at temperatures ranging from 500 to 1100 °C with no hold time or sintered at 1100 °C for 4 h.

Spark plasma sintering experiments were performed in a Dr. Sinter 2050 (Sumitomo Coal Mining Co., Japan) SPS apparatus. The powder was loaded into a graphite die with an inner diameter of 12 mm and prepressed to 100 MPa before heating. The temperature was increased to 600 °C within 3 min, after which a heating rate of 100 °C min^{-1} was applied. At 600 °C the pressure on the powder was increased to 300 MPa (the same pressure as for CIPing) or, for the sake of comparison, to 200 and 500 MPa. The final SPS temperature, in the range from 800 to 1000 °C, was maintained for 3 min. The temperature was monitored using both a thermocouple and an optical pyrometer. The pressure was released when the cooling started from the SPS temperature.

The pore size distribution in the pressed and partially sintered bodies was determined by mercury intrusion porosimetry (Pascal 440, Porotec, Germany). The relative densities of the green and sintered bodies were determined by the Archimedes technique using the value 6.12 g cm^{-3} for the theoretical density of 1.5 YSZ ceramics. The grain size was calculated using the linear intercept method (without any correction factor) on scanning electron microscopy (SEM) micrographs of polished and thermally etched samples.

The dependence of relative density on the sintering temperature during pressureless sintering of nanoparticle compacts is shown in Figure 1. The relative density of the green body started to increase at 700 °C and reached 88% at 1100 °C. After sintering at 1100 °C for 4 h the relative density of the zirconia body reached 98.6% and the intercept grain size was 116 nm (Fig. 2 and Table 1). The temperature of 1100 °C can be regarded as the maximum sintering temperature for 1.5 YSZ zirconia nanopowder. Increasing the sintering temperature caused further grain coarsening, which resulted in the spontaneous transformation of the tetragonal phase to a monoclinic phase during cooling and cracking of the ceramics. The pore size changes in the green

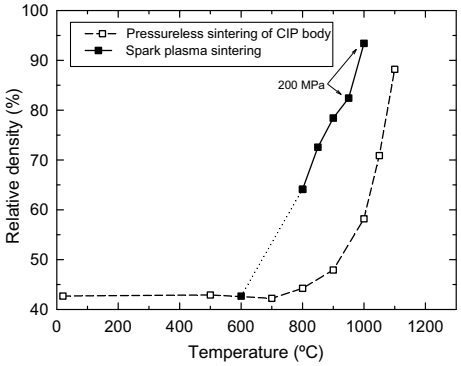

Figure 1. Relative density of nanozirconia compacts densified by SPS and pressureless sintering.

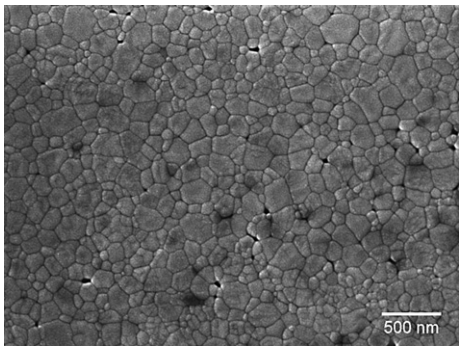

Figure 2. SEM micrograph showing the microstructure of the sample densified by pressureless sintering at 1100 °C for 4 h.

bodies during pressureless sintering are given in Figure 3. The pore size distribution was unimodal in all samples. From the viewpoint of sintering, such a regular distribution can be described using two characteristic pore sizes, namely, the largest pore size and the most frequent pore size. A moderate increase in characteristic pore sizes was already observed at temperatures up to 700 °C; above this temperature the increase was steeper. The pores reached the maximum size (24 nm for the largest pore size and 21 nm for the most frequent pore size) in the temperature range of 1000–1050 °C and were more than twice the original size. Above this temperature the pores began to decrease and close.

The relative density of zirconia nanoceramics densified by SPS reached values comparable to those sintered without pressure at lower temperatures (see Fig. 1). The SPS body densified at 1000 °C and 200 MPa reached a relative density of 93.4%. The relative density could be increased to 99.4% by increasing the SPS pressure up to 500 MPa (Table 1). The intercept grain size of the latter sample was 70 nm (Fig. 4 and Table 1). The pore size evolution during the SPS process was different from pressureless sintering (see Fig. 3). The pore size started to decrease at 800 °C with a minimum growth before this temperature. The density and pore size of bodies densified by SPS at 600 °C could not be determined. We suppose that the value of density was not lower and the values of pore sizes were not higher than the corresponding values found for pressureless sintering.

The above-mentioned results clearly show that zirconia bodies prepared by SPS could reach a higher final density than bodies sintered without pressure (99.4 vs. 98.6% t.d.). The difference of 0.8% can be regarded as significant when approaching the fully dense structure [2]. In addition, the lower SPS temperature and shorter sintering time (minutes in SPS vs. hours in pressureless sintering) resulted in a substantially smaller grain size compared to pressureless sintering (see Figs. 2 and 4).

The advantage of the SPS process at low and intermediate density range can be explained by the pore size changes in the green body. The huge pore size increase during pressureless sintering demonstrates the inhomogeneous packing of nanoparticles in the CIPed compact [2,10]. On the other hand, by rearranging the particles, the SPS technique effectively suppresses the pore size increase and in this way facilitates the sintering process. Trunec and Maca [2] showed that a nanoparticle body