Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 38 (2012) 39–43
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Improvement of microstructural properties of 3Y-TZP materials by conventional and non-conventional sintering techniques

Amparo Borrell [a,*], María Dolores Salvador [b], Emilio Rayón [b], Felipe L. Peñaranda-Foix [c]

[a] Centro de Investigación en Nanomateriales y Nanotecnología (CINN) (Consejo Superior de Investigaciones Científicas – Universidad de Oviedo – Principado de Asturias), Parque Tecnológico de Asturias, 33428 Llanera (Asturias), Spain
[b] Instituto de Tecnología de Materiales (ITM), Universidad Politécnica de Valencia, Camino de Vera, s/n, 46022 Valencia, Spain
[c] Instituto de Aplicaciones de las Tecnologías de la Información y de las Comunicaciones Avanzadas (ITACA), Universidad Politécnica de Valencia, Camino de Vera, s/n, 46022 Valencia, Spain

Received 30 May 2011; received in revised form 14 June 2011; accepted 15 June 2011
Available online 23rd June 2011

Abstract

3 mol% Y_2O_3-stabilized zirconia nanopowders were fabricated using various sintering techniques; conventional sintering (CS) and non-conventional sintering such as microwave (MW) and pulsed electric current-assisted-sintering (PECS) at 1300 °C and 1400 °C. A considerable difference in the densification behaviour between conventional and non-conventional sintered specimens was observed. The MW materials attain a bulk density 99.4% theoretical density (t.d.) at 1300 °C, while the CS materials attain only 92.5% t.d. and PECS 98.7% t.d. Detailed microstructural evaluation indicated that a low temperature densification leading to finer grain sizes (135 nm) could be achieved by PECS followed by MW with an average sintered grain size of 188 nm and CS 225 nm. It is believed that the high heating rate and effective particle packing are responsible for the improvements in these properties.

Keywords: A. Sintering; B. Grain size; B. Microstructure; D. ZrO_2

1. Introduction

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]. Due to the excellent properties, such as low thermal conductivity, excellent biocompatibility, high fracture toughness and strength, high crack resistance and low wear rates, the Yttria-stabilized Tetragonal Zirconia Polycrystalline (Y-TZP) ceramic materials, are widely used for many applications [2].

Therefore, a variety of approaches in the field of sintering have arisen due to the widespread demand of ceramics in recent decades. Hence, understanding how the processing variables affect microstructural evolution is the key to initiating a proper sintering procedure. Various sintering methodologies based on diverse mechanisms are currently available to engineer the densification kinetics enabling the realization of above cited objectives. Applying a promising sintering procedure is, therefore, of a great importance for the superior performance of zirconia bodies. Conventional sintering techniques (hot pressing, sinter forging, hot isostatic pressing, etc.) and non-conventional sintering techniques (pulsed electric current-assisted sintering and microwave) represent an alternative approach to the densification of nanoparticles. In ceramic materials, the high temperatures required to fully densify ceramic powders result in large grain sizes due to Ostwald ripening when traditional sintering techniques are used. This makes it extremely difficult to obtain dense materials with nanometric and submicrometric grain sizes [3]. To overcome the problem of grain growth, non-conventional sintering methods have been proposed in this work.

Pulsed electric current-assisted sintering simultaneously applies pulsed electrical current and pressure directly on the sample leading to densification at relatively lower temperatures and short retention times [4–6]. As both the die and sample are

* Corresponding author. Tel.: +34 985 980 058; fax: +34 985 265 574.
E-mail address: a.borrell@cinn.es (A. Borrell).

0272-8842/$36.00.
doi:10.1016/j.ceramint.2011.06.035

directly heated by the Joule effect extremely high heating rates are possible due to which non-densifying mechanisms like surface diffusion can be surpassed. This technique is widely explored for the development of 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 [7,8].

Microwave radiation for sintering of ceramic components has recently appeared as a newly focused scientific approach [9–16]. Microwave sintering has several advantages such as rapid end volumetric heating, improved production rate, enhancement in densification and grain growth prohibition of ceramics [17–19]. This technique generally uses a frequency of 2.45 GHz resulting in relatively rapid heating rates with uniform grained microstructures and has been employed for the sintering of a wide variety of ceramics ranging from dielectric materials to transparent ceramics. Microwave heating of these materials results from the absorption by molecular vibration (rotating electric dipole/dipole reorientation) and ionic conduction of a portion of the energy transported by an oscillating electric field [11]. A genuine ''microwave effect'', i.e. the acceleration of diffusion mechanisms by the oscillating electric field, was also proposed by some authors to explain the enhancement of the sintering process [11,16,20,21].

The objective of the present study is therefore a comparative evaluation of the densification, microstructure development and mechanical properties in yttria-stabilized zirconia ceramics by the different sintering methodologies: conventional sintering (CS), microwave sintering (MW) and pulsed electric current-assisted sintering (PECS).

2. Experimental procedure

The raw material used in this study was commercial ZrO_2 (3Y-TZP-B) nanopowders (Tosoh Corp., Japan) with average particle size of 50–60 nm. The MW and CS specimens were prepared by uniaxial pressing at 200 MPa of pressure in a steel cylindrical die (2.5 mm thick, 10 mm ϕ). The green density was approximately 2.9 g cm^{-3}, i.e. 49% of theoretical density (6.08 g cm^{-3}). Before MW sintering, the binder of the nanopowders was burnt out under air in an electric furnace by heating at 5 °C min^{-1} up to 600 °C and by soaking for 3 h. The weight loss and shrinkage were about 0.5% and 20%, respectively. This preliminary debinding stage is necessary, since we observed crack development during microwave heating for other specimens. After, all samples were sintered by different methods at 1300 °C and 1400 °C of final temperature.

Zirconia exhibits low dielectric losses at room temperature (~0.04) and increases markedly to ~1000 around 1000 °C. This combined with low thermal conductivity ~2 W m^{-1} K^{-1} and high thermal expansion ($\alpha = 10^{-6}$ K^{-1}) suggest that thermal stresses resulting from non uniform and/or fast heating may cause warpage/cracking. Therefore, SiC crucible with a high dielectric loss must be used as a susceptor in heating by microwave. Green samples were sintered in an experimental microwave oven with 800 W of power and 2.45 GHz of frequency in microwave mono-mode rectangular cavity (Fig. 1). This resonant cavity is coupled by an iris which dimensions are optimized for this application. The method to tune and detune the cavity consists of a sliding short circuit that can be moved electronically, depending on the reflected and consumed power and on the material temperature. The temperature was measured with an optical pyrometer (Optris GmbH, Germany) through a circular hole located on the top of the cavity.

The microwave sintered samples were heated with a heating rate of 30 °C min^{-1} and a holding time of 10 min. Other non-conventional technique is pulsed electric current-assisted sintering, where the powder was placed into a graphite die with an inner diameter of 20 mm and cold uniaxially pressed at 30 MPa. Then, they were introduced in a pulsed electric-current pressure sintering HP D 25/1 (FCT Systeme GmbH, Germany) under low vacuum (10^{-1} mbar). The holding time was to 1 min at the maximum temperature under an applied pressure of 80 MPa and a heating rate of 100 °C min^{-1}. The conventional heating process was carried out in an electrical furnace (Thermolyne type 46100) with 5 °C min^{-1} heating rate and 1 h of holding time.

The density was measured by the Archimedes method (ISO-3369). In order to investigate sample microstructure, polished sections (Struers, model RotoPol-31) with diamond to 1 μm roughness, were thermally etched between 30 min in an electrical furnace under air 100 °C below their maximum sintering temperature to reveal their microstructure. These sections have been observed using a field emission scanning electron microscope (FE-SEM, S4100 HITACHI). The grain size of the sintered samples was determined by multiplying the average linear intercept by 1.56 [22]. For each specimen, at least 15 lines were taken, and their average was reported.

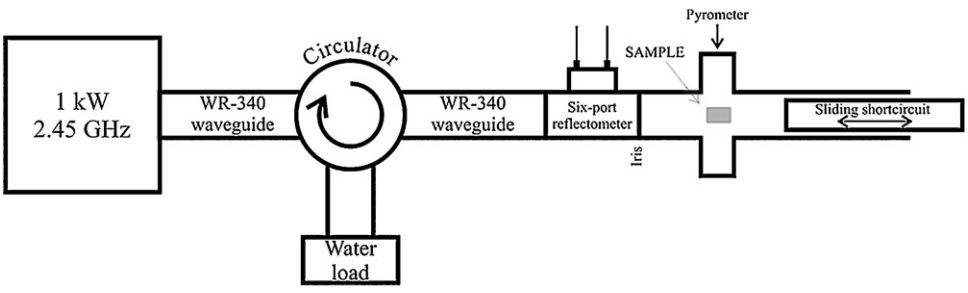

Fig. 1. Microwave system setup.

Table 1
Sintering parameters, sintered densities and average grain size of the 3Y-TZP materials.

Sintering technique	Final temperature (°C)	Dwell time (min)	Relative density (% t.d.)	Average grain size (nm)
CS	1300	60	92.5 ± 0.5	165 ± 5
	1400	60	98.3 ± 0.5	256 ± 3
MW	1300	10	99.4 ± 0.5	188 ± 6
	1400	10	99.9 ± 0.5	225 ± 4
PECS	1300	1	98.7 ± 0.5	135 ± 6
	1400	1	99.0 ± 0.5	245 ± 5

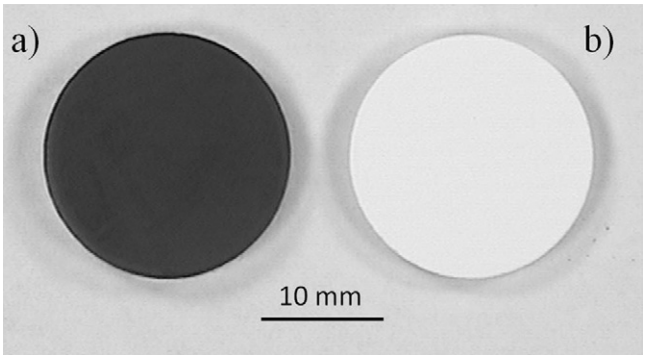

Fig. 2. (a) 3Y-TZP sample sintered by PECS and (b) 3Y-TZP sample sintered by PECS after heating treatment.

3. Results and discussion

Table 1 shows the sintering parameters, relative densities and average grain size of 3Y-TZP powders densified using the sintering methodologies of CS, MW and PECS. It can be observed, a meaningful difference between the relative densities of the conventionally sintered samples and those prepared by MW and PECS.

At 1300 °C, the density of the MW sample was significantly higher than that of the CS and PECS samples. At this temperature if we compare the samples sintered by MW with 10 min of dwelling time and CS with 1 h of dwelling time, the MW sample has a density enhancement up to 7% (from 92.5% to 99.4%) in a shorter time.

On increasing the temperature to 1400 °C a significant improvement in densification is observed in the CS samples. On the other hand, the MW method shows full dense samples compared to the pressed compacts sintered by PECS at equivalent temperatures. Therefore, maximum densification was provided by MW, wherein samples could be sintered to >99.9% at a temperature of 1400 °C for 10 min. According to previous reports [16,19], microwave heating has been recognized as a promising method to improve the densification in the same ceramic systems.

During microwave heating energy is transferred to the material electro-magnetically and not as a thermal heat flux

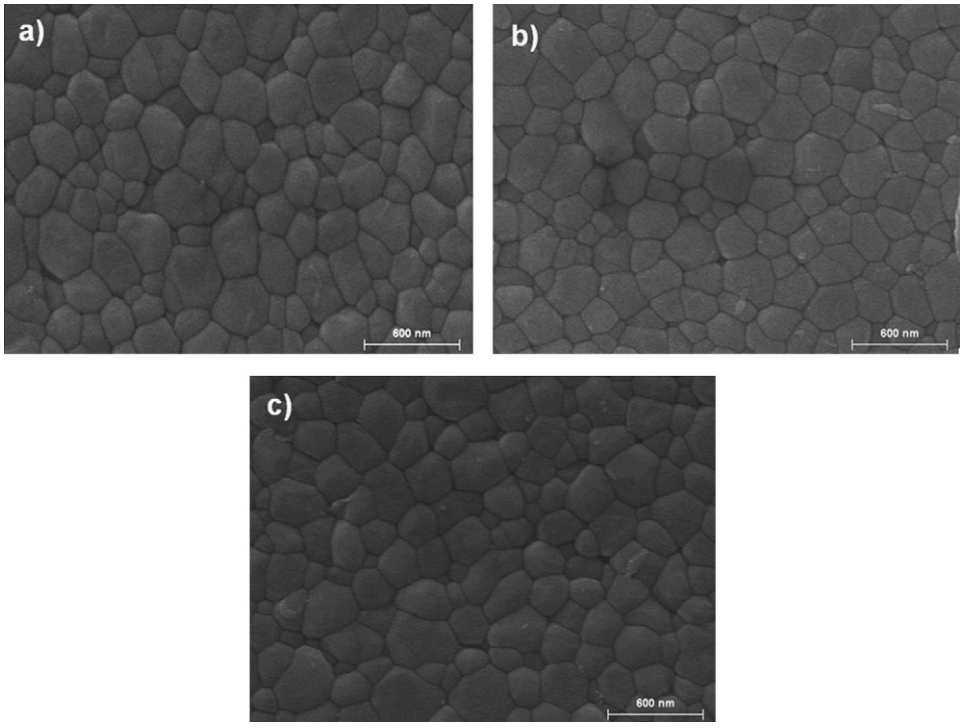

Fig. 3. FE-SEM micrographs of near full dense specimens sintered by PECS at 1400 °C/1 min (a), MW at 1400 °C/10 min (b), and CS at 1400 °C/60 min (c).

enabling the material to be heated at rapid rates. The higher oxygen vacancies associated with 3 mol% yttria-stabilized zirconia provide higher ionic conductance at elevated temperatures leading to high dielectric losses and enhanced absorption of microwaves. This mechanism could be one possible reason for the shorter sintering times in MW.

The rapid densification of samples by PECS is attributed to the enhanced densification rate due to mechanisms such as particle rearrangement and the breaking up of agglomerates aided by applied pressure and faster heating rates. By rearrangement of particles, the PECS process also impedes the pore size increasing which was generally observed in the first and intermediate stages of sintering. Further, applied electric field also promotes the diffusion of ions and vacancies which enhances the sintering rate.

But this method has a big problem with the sintering of zirconia materials. As can be observed in Fig. 2a, the sample sintered by PECS at 1300 °C shows a full black colour. This is due to carbon diffusion within the zirconia sample by PECS processing, which is linked to the carbon rich atmosphere in which it is performed. As the sintering of the compact is taking place in a graphite die, the carbon diffuses into the sample from the die and this process is promoted by the applied pressure. Eliminating this contamination is possible (Fig. 2b), but this implies high temperatures (>800 °C) and a long time inside a furnace (>2 h), resulting in high economic costs.

Fig. 3 represents the FE-SEM microstructure of 3Y-TZP samples sintered by PECS, MW and CS at 1400 °C. All the sintered specimens exhibited equiaxed grain microstructures and the average grain size varied over a wide range from 135 nm to 256 nm.

Nanocrystalline 3Y-TZP ceramics with average grain size of 225 nm and a complete elimination of residual porosity were obtained at 1400 °C for 10 min by MW. The CS samples revealed a slight grain growth with an average grain size of 256 nm, and the PECS of 245 nm. These microstructures show similar values of grain size, but the MW micrograph (Fig. 3b) shows a better homogeneous microstructure than the PECS and CS ones. Therefore, application of a heating microwave method has provided traces of improvement for grain growth suppression and densification compared to the other sintering techniques employed.

4. Conclusions

The microstructural evolution of the nanometric 3Y-TZP powder subjected to different sintering techniques (MW, PECS and CS) has been carried out in the current investigation. Comparison with conventional sintering shows that microwave sintering has a number of benefits in terms of microstructural design. Zirconia powders sintered by the microwave technique at the temperature of 1400 °C show a full density of 99.9% at an average grain size of 225 nm with a more homogeneous microstructure compared to the specimen conventionally sintered at the same temperature.

Acknowledgements

This work has been carried out with programme to support research and development of the Polytechnic University of Valencia (U.P.V) under multidisciplinary projects PAID-05-09 and PAID-05-10. A. Borrell, acknowledges the Spanish Ministry of Science and Innovation for her FPI Ph.D. grant and the people from Institute Technological of Materials (ITM) of the U.P.V for helping us with the microwave experiments during a stay in 2010–2011. Felipe L. Peñaranda-Foix wants to thank the Generalitat Valenciana for the grant obtained in the frame of the Program BEST/2010, because some results of this paper have been possible with this help.

References

[1] M.J. Mayo, Processing of nanocrystalline ceramics from ultrafine particles, Int. Mater. Rev. 41 (1996) 85–115.
[2] S. Deville, L. Gremillard, J. Chevalier, G. Fantozzi, A critical comparison of methods for the determination of the aging sensitivity in biomedical grade yttria-stabilized zirconia, J. Biomed. Mater. Res. B: Appl. Biomater. 72 (2005) 239–245.
[3] U. Anselmi-Tamburini, J.E. Garay, Z.A. Munir, Fast low-temperature consolidation of bulk nanometric-ceramic materials, Scripta Mater. 54 (2006) 823–828.
[4] L. Gao, Z.J. Shen, H. Miyamoto, M. Nygren, Superfast densification of oxide/oxide ceramic composites, J. Am. Ceram. Soc. 82 (1999) 1061–1063.
[5] T. Nishimura, M. Mitomo, H. Hirotsuru, M. Kawahara, Fabrication of silicon nitride nano-ceramics by spark plasma sintering, J. Mater. Sci. Lett. 14 (1995) 1046–1047.
[6] M. Yoshimura, T. Ohji, M. Sando, K. Niihara, Rapid rate sintering of nano grained ZrO_2-based composites using pulse electric current sintering method, J. Mater. Sci. Lett. 17 (1998) 1389–1391.
[7] R. Chaim, Superfast densification of nanocrystalline oxide powders by spark plasma sintering, J. Mater. Sci. 41 (2006) 7862–7871.
[8] R. Chaim, Densification mechanisms in spark plasma sintering of nanocrystalline ceramics, Mater. Sci. Eng. A 443 (2006) 25–32.
[9] A. Goldstein, N. Travitzky, A. Singurindy, M. Kravchik, Direct microwave sintering of yttria-stabilized zirconia at 2.45 GHz, J. Eur. Ceram. Soc. 19 (1999) 2067–2072.
[10] P. Both, N. Lequeux, Do microwaves increase the treatment sinterability of ceramic? Solid State Ionics 101–103 (1997) 1229–1233.
[11] D.D. Upadhaya, A. Ghosh, K.R. Gurumurthy, R. Prasad, Microwave sintering of cubic zirconia, Ceram. Int. 27 (2001) 415–418.
[12] M. Mizuno, S. Obata, S. Takayama, S. Ito, N. Kato, T. Hiraia, M. Sato, Sintering of alumina by 2.45 GHz microwave heating, J. Eur. Ceram. Soc. 24 (2004) 387–391.
[13] J. Raabe, E. Bobryk, V. Petrovsky, Fabrication of mullite–zirconia composites by microwave sintering of corundum/amorphous silica particles and sol–gel substrates, Ceram. Int. 27 (2001) 81–84.
[14] T. Ebadzadeh, M.H. Sarrafi, E. Salahi, Microwave-assisted synthesis and sintering of mullite, Ceram. Int. 35 (2009) 3175–3179.
[15] M.L. Sandoval, M.H. Talou, P.M. de Souto, R.H.G.A. Kiminami, M.A. Camerucci, Microwave sintering of cordierite precursor green bodies prepared by starch consolidation, Ceram. Int. 37 (2011) 1237–1243.
[16] J. Wang, J. Binner, B. Vaidhyanathan, N. Joomun, J. Kilner, G. Dimitrakis, T.E. Cross, Evidence for the microwave effect during hybrid sintering, J. Am. Ceram. Soc. 89 (2006) 1977–1980.
[17] T. Ebadzadeh, M. Valefi, Microwave-assisted sintering of zircon, J. Alloys Compd. 448 (2008) 246–251.
[18] C. García-Gañan, J.J. Meléndez-Martínez, D. Gómez-García, A. Domínguez-Rodríguez, Microwave sintering of nanocrystalline Ytzp (3 mol%), J. Mater. Sci. 41 (2006) 5231–5234.

[19] J. Cheng, D. Agrawal, Y. Zhang, R. Roy, Microwave sintering of transparent alumina, Mater. Lett. 56 (2002) 587–592.
[20] S.A. Nightingale, D.P. Dunne, H.K. Worner, Sintering and grain growth of 3 mol% yttria zirconia in a microwave field, J. Mater. Sci. 31 (1996) 5039–5043.
[21] S.A. Nightingale, H.K. Worner, D.P. Dunne, Microstructural development during the microwave sintering of yttria-zirconia ceramics, J. Am. Ceram. Soc. 80 (1997) 394–400.
[22] Y. Wang, Z. Fu, Study of temperature field in spark plasma sintering, Mater. Sci. Eng. B 90 (2002) 34–37.