Sintering Properties of ZrO_2 - 3 Mol % Y_2O_3 Obtained from Mixture of Nano and Microcrystalline Powders

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Abstract: The polymeric precursor route based on the Pechini process was used to prepare a mixture of nano and microcrystalline powders. The zirconia powder was stabilized with 3 mol% of yttria. Powder characteristics were evaluated by the BET technique determined the specific area and the BJH method supplied the pore size distribution. The X-ray diffraction results and SEM observations were carried out to characterize both the powder mixture and the microstructures of the ceramic bodies. The sintering behavior shown in this work was studied by dilatometric experiment, being considered the shrinkage rate, densification and grain size of the microstructure.

Introduction

The use of advanced ceramics finds a wide field of applications in the structural area. A powder with appropriate physical (small grain size, narrow size distribution, low agglomeration) and chemistry (composition and homogeneity) characteristics is necessary to obtain a structural ceramic with compatible mechanical properties in agreement with its use. Zirconia ceramics are very known materials for structural applications. In particular, its characteristic tetragonal phase is indicated for this field, motivated by the excellent strength and toughness properties exhibited at room temperature. This special property is due to the stress-induced transformation from the tetragonal to monoclinic phase, which is accompanied of an increase in the grain volume that provokes an intern compression state in the material. [1,2]. But zirconia is usually monoclinic at room temperature. The stabilization of the tetragonal phase is made with the addition of certain oxides, like CaO, CeO2, MgO, and Y_2O_3.

Yttria doped zirconia has been motivated several studies, mainly in the synthesis of powders with nanometric size particles [3-5]. Among the benefits of the use of nanometric powders the decrease of the sintering temperature and the obtaining of ceramic can be mentioned with more homogeneous and dense microstructures To produce ceramic with these characteristics, different methods and their variations, in that are included hydrothermal synthesis [6], coprecipitation [7-9], sol-gel [10,11], and inert gas condensation [12,13], are employed.

The polymeric precursor technique, also known as the citrate process, is an effective route for preparation of nanopowder. Many years ago Pechini investigated a preparation of simple powder for polymeric precursors starting from citric acid and ethylene glycol [14]. In this process, an alpha hydroxycarboxylic acid (usually citric acid) it is used to form chelates with several cationic precursors forming a polybasic acid. When mixing with a polyhydroxylic alcohol (as ethylene glycol) these chelates react to form organic esters and water. When the mixture is heated, polyesterification happens and conducts to a homogeneous sol, maintaining metal ions evenly distributed throughout the organic matrix. The sol is further heated to remove the excess of solvents yielding a high viscous polyester resin. The solid resin is then submitted to high temperatures to remove organic residues and the wanted stoichiometric combinations are formed during the pyrolysis. Besides larger homogeneity and purity of the product, the sol-gel method allows a low

process temperature and a morphologic control of crystalline particle of uniform size in extra fine dimensions.

The purpose of the present study is to prepare a zirconia powder with 3 mol % of yttria to stabilize the tetragonal metastable phase, using the Pechini method for the production of nanometric particles mixture with micrometric powder, and particularly to observe the powder sintering properties in dilatometry test. The objective of the mixture of powders with different particle sizes is to use the nanoparticles to cause joining of the microparticles during the sintering step.

Experimental

Zirconia powder was obtained by the Pechini method. Zirconium chloride and yttrium chloride were used as precursors of the citrate solution. ethylene glycol and citric acid were used for polymerization of the process. Firstly, the citric acid (CA) was dissolved in the deionized water and maintained under agitation at approximately 80°C. Then, appropriated amounts of zirconium oxychloride ($ZrOCl_2.8H_2O$) and yttrium chloride were added and they were maintained under constant agitation and temperature, until the homogenization of the solution. The pH chosen (value of 8) was kept constant by controlled addition of ammonia hydroxide. Next, the ethylene glycol was increased (EG) in the proportion CA/EG 1:4, being maintained the stirring and the temperature of 80°C. The polyesterification reaction happened after 8 hours of heating, resulting in a viscous solution in which the micrometric commercial zirconia powder purchased from Zhongshun Sci.&Tec. Co. was added. The micrometric powder was composed by particles with sizes ranging from 0.5 to 10 μm. The mixture continued in constant agitation and temperature for several hours, and later was dried at 300 °C to eliminate the organic matter. The drying of the gel resulted in a black solid product that was easily triturated using mortar and pestle. The calcination was made at 500 °C during 10 hours. Compacts were done by firstly using uniaxial compaction at 60 MPa, followed by cold isostatic pressing at 300 MPa.

Nitrogen adsorption technique (Quantachrome 1000) was used for the determination of pore size distribution through the BJH method and specific surface area by BET method. Prior to each analysis, powder samples were out-gassed for 2 hours at 200°C to remove possible pollutant of the powder surface. Powder morphology was observed by scanning electron microscopy – SEM (Jeol JMS 5310). X ray diffraction (Philips PW1840) was used to phase determination in the powder using Cu Kα radiation at40 kV and 25 mA and a scan rate of 0.02 °.min^{-1}. The sintering study was carried out in a dilatometer (Netsch-DIL 402E/7). The heating rate was 10 °C.min^{-1} up to 1550 °C, using a compact made under uniaxial pressing of 250 MPa.

Results and Discussion

The powder mixtures processed was calcined at 500 °C/10 h, according to results obtained from thermal analysis.

The dried powder was not amorphous as determined by X-ray diffraction (Fig. 1), displaying the presence of the monoclinic phase of the zirconia. This monoclinic phase is related to the powder composed of micrometric particles that was mixed to the nanometric powder during its preparation. The amount of yttria added should react in both the powders, stabilizing the tetragonal phase. After powder calcination at 500 °C is noticed the presence of peaks corresponding to the tetragonal phase of the zirconia amid the predominance of the monoclinic peaks.

The specific area measured by BET method is 90.44 m^2/g. This value of specific area presented a powder with elevated reactivity, an important factor that helps to reduce the sintering temperature.
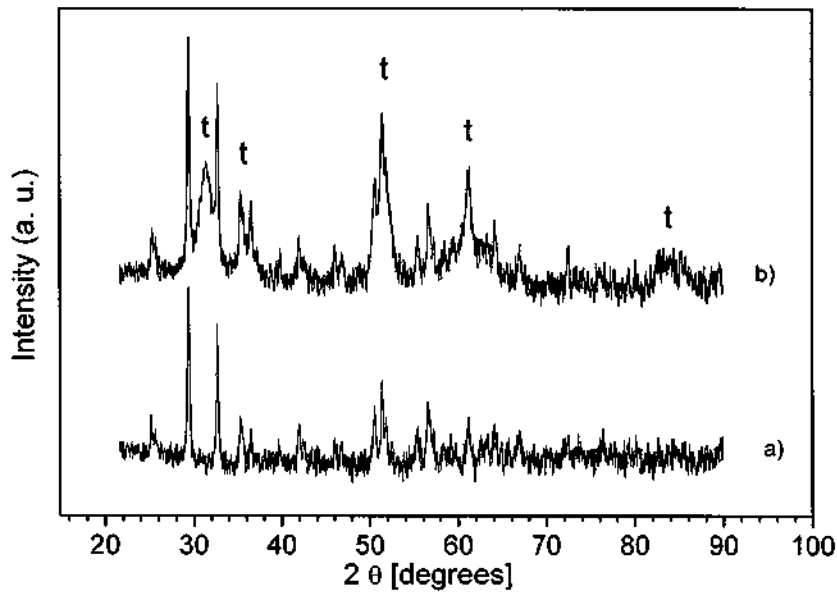
Fig. 1 XRD for the ZrO₂ -3 mol % Y₂O₃ powder: a) dried, b) calcined at 500°C. "t": tetragonal zirconia. All non specified peaks related to monoclinic zirconia

The porosity distribution in the calcined powder is presented in Figure 2. As can be seen, the pore size distribution is formed by very fine pores that extend in the range of 1.74–9 nm. Pores in the range of 2.6–5.8 nm constituted the largest part of the porous volume, with a maximum at 3.6 nm. This pore distribution is attributed to interagglomerate pores that were formed during the calcination. The average pore diameter is 4.4 nm.
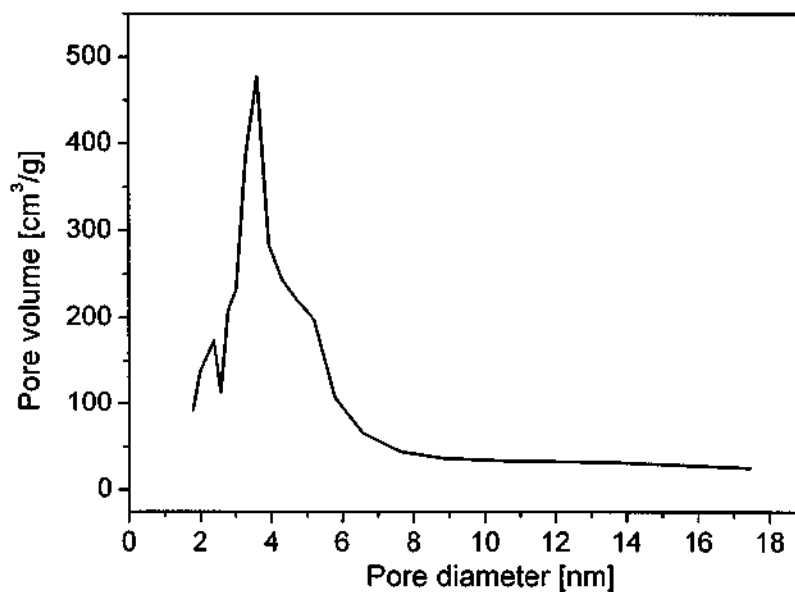

Fig. 2 Pore size distribution of ZrO₂ -3 mol % Y₂O₃ powder.

The powder morphology of the calcined powder was observed by SEM micrographs (Fig. 3). The mixture of the nano and micrometric particles resulted in the formation of agglomerates with no shape uniformity and with a wide distribution of sizes, some of them about 10 μm (Fig. 3a). Along the agglomerates particles in the nanometric scale can be seen (Fig. 3b).

Dilatometric experiment in air was carried out in calcined powder to observe the linear shrinkage and its derivative curve respectively (Fig. 4). From room temperature up to 540 °C, when
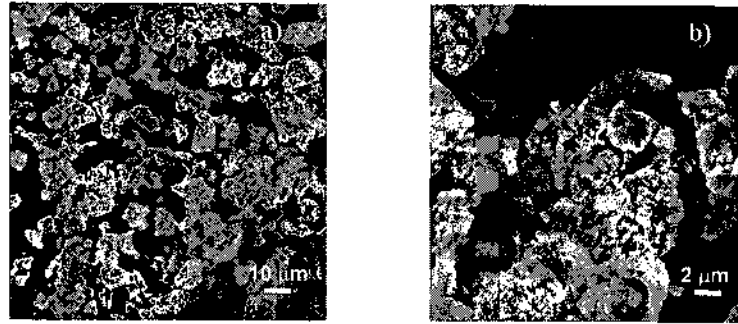
Fig. 3 SEM micrographs of ZrO_2 -3 mol % Y_2O_3 calcined powder: a) 1000X, b) 5000X

the compact starts to shrink, no shrinkage is verified. In the interval temperatures of 540 to 1160 °C occurs a slight retraction which can be attributed to the accommodation and formation of the particle contacts. Starting from 1160 °C a higher shrinkage rate of the compact happened, being related to the gradual elimination of porosity and the grain growth action. The total shrinkage reaches 18.40 % at 1550 °C. The maximum densification rate is found at a temperature of 1390 °C.
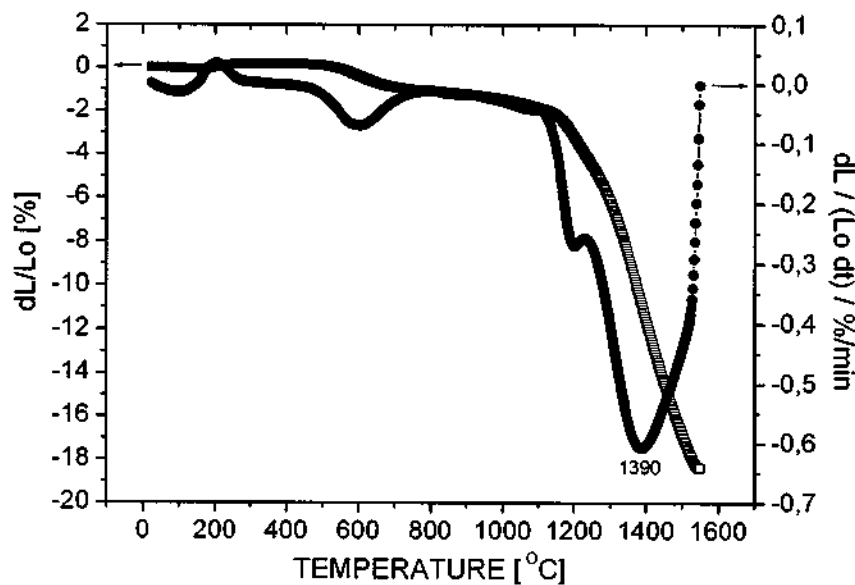

Fig. 4 Sintering behavior of the ZrO_2 -3 mol % Y_2O_3 observed in dilatometric experiment

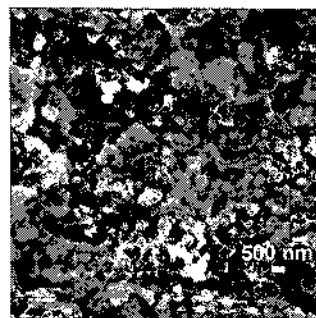Fig.5 presents the fracture surface of a sample sintered at 1400 °C during 3 h.

Fig. 6 Microstructure of the fracture surface in ZrO_2 -3 mol % Y_2O_3 sintered specimen.

Conclusions

Acknowledgement

References

[1] Garvie, R.C. *Journal of Material Science,* n. 20 (1985), p. 3479-3486.

[2] Stevens, R. *Trans. Brit. Ceram. Soc.,* n. 80 (1981), p. 81-85.

[3] Robert, C.L.; Ansart, F.; Deloget, C.; Gaudon, M. and Rousset, A. *Ceram. Int.,* v. 29 (2003), p. 151-158.

[4] Lamas, D.G.; Lascalea, G. E. and De Reca, N. E. W. *J. Eur. Ceram. Soc.,* v.18 (1998), p. 1217-1223,.

[5] Quinelato, A.L.; Longo, E.; Perazolli, L.A.; Varela, J.A. *J. Eur. Ceram. Soc.,* v. 20 (2000), p. 1077-1084.

[6] Dell'Agli, G.; Mascolo, G. *J. Eur. Ceram. Soc.,* v. 20 (2000), p. 139-145.

[7] Qiu, H. B.; Gao, L.; Qiao, H. C.; Guo, J. K. and Yan, D. S. *Nanostruct. Mat.,* v. 6, (1995), p. 373-376,.

[8] Vijayakumar, M; Selvasekarapandian, S. et-al. *Physica B,* v. 334 (2003), p. 390–397.

[9] Qian, Z. and Shi, J .L. *Nanostruct. Mat.,* v. 10, n. 2, (1998), p. 235-244.

[10] Liu, W.; Chen, Y., Ye, C.; Zhang, P. *Ceram. Int.,* v. 28 (2002), p. 349–354.

[11] Srdic, V. V.; Omorjan, R.. P., *Ceram. Int.,* v. 27 (2001), p. 859–863.

[12] Nitsche, R.; Winterer, M.; and Hahn, H. *Nanostruct. Mat.,* v. 6 (1993), p. 679-682.

[13] Betz, U.; Sturm, A.; Loeffler, J. F.; Wagner, W.; Wiedenmann, A. and Hahn, H. *Nanostruct. Mat.,* v. 12 (1999), p. 689-692.

[14] Pechini, M.P. *US Patent n. 3 330 697,* 1967.