Hydrothermal treatment of coprecipitated YSZ powders

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Keywords: yttria stabilized zirconia, synthesis, coprecipitation, hydrothermal treatment

Abstract. Zirconia stabilized with 8.5 mol% yttria (YSZ) were synthesized by coprecipitation and resulting gels were hydrothermallly treated at 200°C and 220 PSI for 4, 8 and 16 hours. Products were oven dried at 70°C for 24 hours, uniaxially pressed as pellets and sintered at 1500 °C for 1 hour. Powders were characterized for surface area with N_2 gas adsorption, X-ray diffraction, laser diffraction granulometric analysis and scanning and transmission electronic microscopy. Density of ceramics was measured by an immersion method based on the Archimedes principle. Results showed that powders dried at 70°C are amorphous and after treatment has tetragonal/cubic symmetry. Surface area of powders presented a significant reduction after hydrothermal treatment. Ceramics prepared from hydrothermally treated powders have higher green density but sintered pellets are less dense when compared to that made with powders calcined at 800°C for 1 hour due to the agglomerate state of powders. Solvothermal treatment is a promising procedure to enhance density.

Introduction

Zirconia is one of the most important high performance ceramics due the possibility of stabilization of high temperature polymorphic phases (tetragonal and/or cubic), at room temperature, employing divalent or trivalent cation as dopants [1]. The addition of 3 mol% of yttria stabilizes tetragonal phase, making possible its uses as structural and bioceramics, due to improved mechanical properties [2-4]. On the other hand, doping with 8-9 mol% of yttria increases oxygen ion conduction at high temperatures (around 1000^{o}C), allowing applications as solid electrolytes in electrochemical devices such as solid oxide fuel cells and oxygen sensors [5,6]. However, to attain these intrinsic properties it is important to control powders synthesis and ceramic processing parameters in order to achieve a homogeneous and dense microstructure [7,8]. Hydrothermal/solvothermal treatment of coprecipitated gels has been considered a good alternative for this purpose because it is a soft chemical route that uses low working temperatures to obtain nanometer sized crystalline powders with weakly bonded agglomerates [9-11]. The term *hydrothermal* was first used to describe the action of water at elevated temperature and pressure, in changes in earth's crust, leading to the formation of various rocks and minerals. Nowadays this definition has undergone several changes from the original meaning and is considered a chemical reaction in the presence of a solvent (aqueous or non-aqueous) above the room temperature and at pressure greater than 1 atm in a closed system. *Solvothermal* term is also employed to describe chemical reaction in the presence of non-aqueous solvent [12].

Taking into account the great importance of powder synthesis processes to a better ceramic performance, it was evaluated in this work, the association of coprecipitation method and hydrothermal treatment for the production of powders and ceramics of zirconia stabilized with 8.5 mol% yttria.

Experimental procedure

The starting material for the solvothermal and hydrothermal studies were coprecipitated zirconium hydroxide as described in details elsewhere [8]. Briefly, it consists on a mixture of zirconium oxychloride and yttrium chloride aqueous solutions that is added to an ammonium hydroxide solution under agitation. The resulting gel is filtered and washed with water in order to eliminate chloride ions. In this work zirconium – yttrium hydroxide gel was submitted to hydrothermal/ solvothermal ageing employing an pressurized reactor (Parr Instruments, 4566 Mini Reactor) according to the following procedures:

(1) hydrothermal ageing in water media at 200^{o}C and 220 psi for 4, 8 and 16 hours and oven-drying at 70^{o}C for 16 hours (HYSZ 4/8/16 samples)

(2) Ageing in ethanol and butanol at 200^{o}C and 270 psi for 16 hours and drying 70^{o}C for 16 hours (HYSZ –16 E/B samples).

(3) Ageing in water or butanol at 200^{o}C and 270 psi for 16 hours, drying 70^{o}C for 16 hours and ball or attrition milling in ethanol media for 16 and 4 hours, respectively (HYSZ-16 M/MA/BM samples).

For comparison purposes, coprecipitated powders submitted to ethanol washing, azeotropic distillation in butanol and drying was also prepared (HYSZ-0). This sample was calcined at 800^{o}C (YSZ-800) for 1 hour and ball milled in ethanol for 16 hours. All these procedures and sample codes are summarized in Table 1. The synthesized ceramic powders were formed as cylindrical pellets by uniaxial pressing and sintered at 1500 °C for 1 hour.

Table 1- YSZ sample code description according coprecipitate gel treatment.

Sample Code	Azeotropic Distillation	Hydrothermal Treatment		Drying	Calcination	Millling
		media	Time (h)			
HYSZ - 0	X	—	—	X	—	—
HZYSZ- 4	—	water	4	X	—	—
HZYSZ - 8	—	water	8	X	—	—
HZYSZ -16	—	water	16	X	—	—
HYSZ-16 E	—	ethanol	16	X	—	—
HYSZ-16 B	—	butanol	16	X	—	—
HYSZ-16 M	—	water	16	X	—	ball
HYSZ-16MA	—	water	16	X	—	Ball/attrition
HYSZ-16 BM	—	butanol	16	X	—	Ball
YSZ - 800	X	—	—	X	X	ball

Powders were characterized by X-ray diffraction for phase identification, transmission electron microscopy (Jeol, JEM 2100) for particle size and morphology observation and gas adsorption (Nova 1200, Quantachrome) for surface area measurements. Thermogravimetric-differential thermal analyses (TG-DTA) of the dried gels were carried out using Setaram Labsys –TG/DTA, under dynamic air and heating rate of 10^{o}C.min^{-1}. Ceramic sinterability was evaluated by dilatometry (Setaram Labsys Instrumentation, TMA) and density measurements by Archimedes method.

Results and discussion

XRD patterns of YSZ powders (Fig.1) shows the crystallization of tetragonal/cubic phase for hydrothermal treated and calcined samples. TEM micrographs of YSZ-800 and HYSZ-16 powders

(Fig.2) indicate that both powders are in nanoscale, although the high degree of agglomeration, shown by SEM (Fig. 3), when milling is not employed.

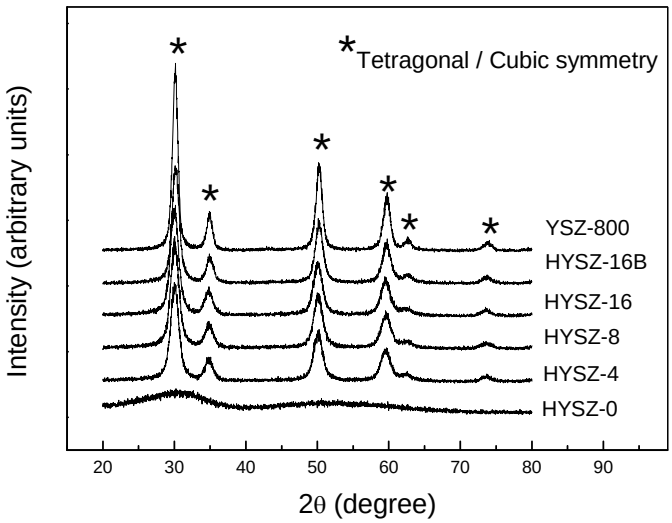


Figure 1: X-ray diffraction patterns of YSZ synthesized powders.

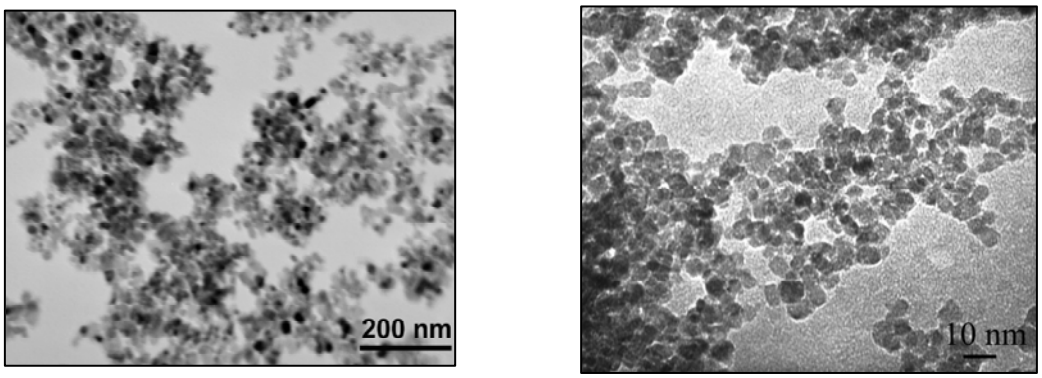


Figure 2.TEM micrographs of calcined and milled powder (a) and hydrothermal treated (b), represented by YSZ-800 and HYSZ-16 samples, respectively.

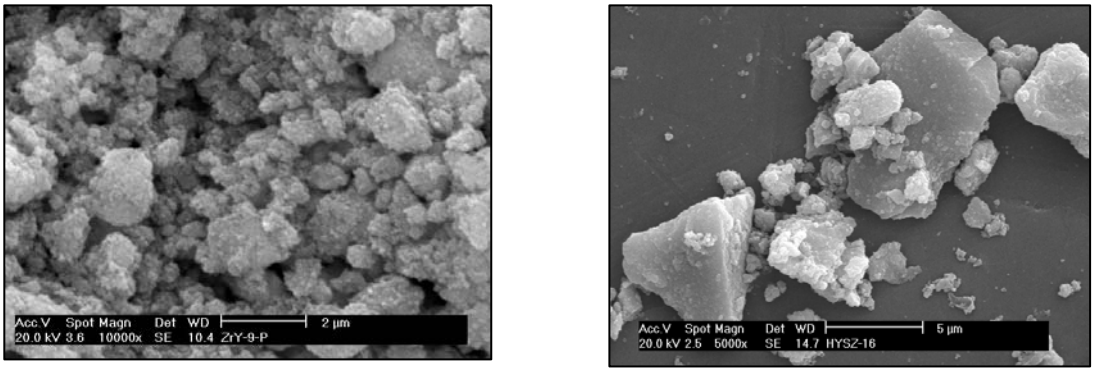
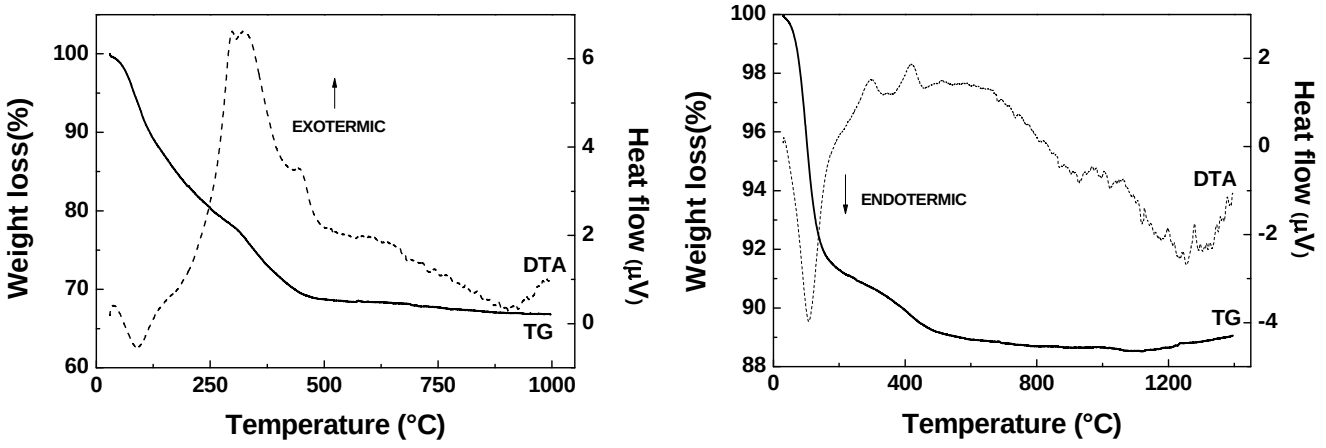


Figure 3.SEM micrographs of calcined and milled powder (a) and hydrothermally treated (b), represented by YSZ-800 and HYSZ-16 samples, respectively.

The TG/DTA results of the thermal decomposition process of HYSZ-0 and HYSZ-16 samples are shown in Fig.4. The weight loss of oven-dried powders occurs in the range of 25-550°C. Elimination of free water and OH^- groups occurs around 100°C (endothermic peak) for both samples. Crystallization of oxide structure, indicated by exothermic peaks near 400°C [8], is more pronounced for HYSZ-0 sample due to the previous oxide formation of HYSZ-16 sample during hydrothermal treatment.



(a) (b)

Figure 4. DTA/TG analysis of synthesized powders: (a) after coprecipitation and drying (HYSZ-0 sample) and (b) after coprecipitation, hydrothermal treatment and drying (HYSZ-16 sample)

Table 2 shows the values of specific surface area of YSZ synthesized powders and the relative densities of resulting ceramics after sintering at 1500°C for 1 hour. It can be observed that hydrothermal treatment reduces surface area of dried powders, but this parameter is not a function of ageing time. However, compared to oxides crystallized by calcination, specific surface area of hydrothermal treated powders are greater.

Table 2: Specific surface area of YSZ powders and relative density of prepared ceramics.

Sample code	Calcination (°C)	Hydrothermal treatment time (hours)	Surface area ($m^2.g^{-1}$)	Relative* density (%)
HYSZ - 0	—	0	319.2	-
HZYSZ- 4	—	4	161.8	86.7
HZYSZ - 8	—	8	175.0	86.0
HZYSZ -16	—	16	173.2	87.5
HYSZ-16 E	—	16	158.3	97.5
HYSZ-16 B	—	16	151.2	97.9
HYSZ-16 M	—	16	148.1	91.8
HYSZ-16MA	—	16	124.9	95.3
HYSZ-16 BM	—	16	153.2	95.3
YSZ - 800	800	0	81.8	96.0

*Relative to 6.01g.cm^{-3}

Relative density values of ceramics indicate that the employment of water for ageing does not promotes densification. Better results were attained for samples treated with ethanol or butanol. Milling procedure was not efficient to density improvement, but values are higher than 95%TD for alcohol hydrothermal treated samples. This behavior is probably due to agglomerate formation during drying and heterogeneous breaking during compaction.

Sintering behavior of the compacted powders in air, under a constant heating rate of 10ºC/min, is shown in Fig. 5. For compacts prepared from calcined powders small or no shrinkage was detected below 1000^{o}C and maximum densification was not reached due to equipment temperature limitation. On the other hand, two shrinkage mechanisms are observed for hydrothermal treated powders: The first one from room temperature until 1100^{o}C is probably related to the remain loss of hydroxyl groups. Above this temperature a continuous shrinkage is observed due sintering process. The complete densification was reached near 1300^{o}C for these samples. Maximum densification rates was observed between 1150and 1200^{o}C for both sample series.

It is important to note that although dilatometric results indicates that sintering process is enhanced by hydrothermal treatment, higher density is only attained by the employment of powder conditioning processes, such azeotropic distillation of coprecipitated hydroxides, solvothermal treatment with butanol and ethanol and milling. Relative density results of Table 2 confirm this observation.

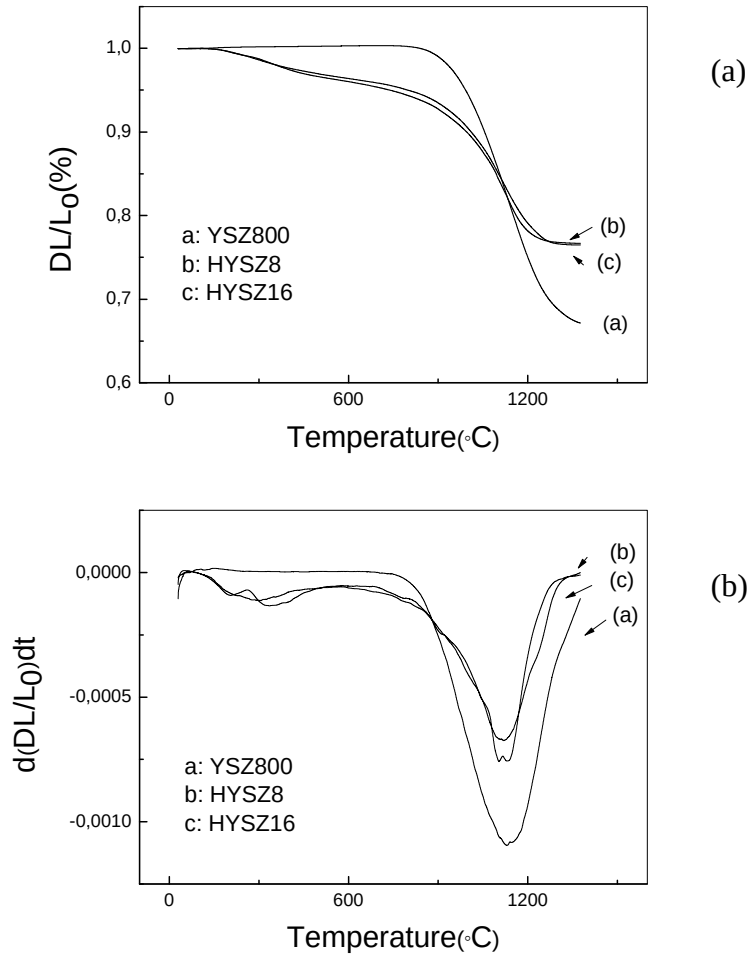


Figure 5. Linear shrinkage (a) and linear shrinkage rate (b) of YSZ compacts prepared from calcined powders (YSZ800) and from hydrothermal treated powders (HYSZ8 and HYSZ16), under 10^{o}C/min heating.

Conclusions

Hydrothermal/solvothermal treatment has been considered a good alternative to improve crystallization of YSZ powders at low temperatures (around 200^{o}C), eliminating calcination process that requires greater power consumption. The obtained powders are in nanometer scale grouped as hard agglomerates when water is used as ageing media. The employment of ethanol and butanol media leads to powders weakly agglomerated and consequently to high density ceramics.

Acknowledgments

The authors would like to thank the CNPq (Project 471491/2007-1) and FINEP (PaCOS network) for the financial support and the scholarship. Thanks also to our colleagues from CCTM/IPEN and PROCEL/IPEN, especially from the Laboratories of Microscopy, XRD and Thermal Analysis.

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