Synthesis of reactive neodymia-doped zirconia powders by the sol–gel technique

E.N.S. Muccillo*, E.C.C. Souza, R. Muccillo

Energy and Nuclear Research Institute, Multidisciplinary Center for the Development of Ceramic Materials-CCTM, C.P. 11.049-Pinheiros-05422-970, S. Paulo, SP, Brazil

Abstract

Zirconia–x mol% neodymia (x=3, 5 and 8) solid solutions were prepared by the sol–gel technique. The aim of this work is to obtain reactive ceramic powders with high structural homogeneity using a simple method of solid solution synthesis. Powder characterization comprises: thermal analyses to study the decomposition behavior of the precursor; laser scattering to obtain the particle size distribution; scanning electron microscopy to observe shape and size of the agglomerated particles; X-ray diffraction experiments on sintered specimens for phase characterization, and dilatometric experiments to obtain the linear shrinkage of a powder compact.
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1. Introduction

ZrO_2–RE_2O_3 (RE=rare earth) solid solutions with ultrafine particles are components of catalytic materials like supports and promoters usually employed in the chemical synthesis and in the control of pollution reactions [1,2]. These solid solutions have also potential application as ionic conductors.

The introduction of rare earth ions in the zirconia structure results in phase stabilization along with the formation of anionic vacancies. The fraction and the type of the formed phase are a function of the cation dopant, its ionic radius and concentration, and of the reactions occurring during processing of the solid solution. For doping levels up to ~3 mol% of RE_2O_3, the tetragonal structure is formed whereas for compositions higher than ~12 mol% the zirconia is fully stabilized in the cubic structure.

Zirconia–rare earth oxide solid solutions may be obtained by solid state reactions as well as by solution techniques. The coprecipitation technique is one of the most used techniques for preparing these solid solutions. Many recent studies have concentrated on the metastability of the tetragonal phase as a function of the cationic radius of the rare earth dopants and of thermal treatments [3–6].

The ZrO_2–Nd_2O_3 system has been already used as a catalytic support for iron oxide for the removal of carbon monoxide at low temperatures [7]. The optimized performance of this system was related to the adsorption of oxygen and carbon monoxide molecules on active sites [8]. For this application, the homogeneity of the structural phase of the solid solution is quite important.

In this work, solid solutions of ZrO_2–xNd_2O_3 (x=3, 5 and 8 mol%) were prepared by the sol–gel technique proposed by Courty et al. [9]. The main purpose was to obtain reactive powders with controlled physical and structural properties using a simple technique for solid solution preparation.

2. Experimental

Hydrated zirconium oxide (>99%) and neodymium oxide (>99.9%), both prepared at our Institute, were used as starting materials. Other reagents were of analytical grade. A stock solution of zirconium nitrate was prepared by slow dissolution of the precursor material in a hot nitric acid solution (1:1). The concentration (134.3 g l^{-1}) of the zirconyl nitrate solution was determined by gravimetry. The neodymium nitrate solution was prepared by dissolving the corresponding oxide in a nitric acid solution (1:1) at room temperature. Further heating of this solution was performed to ensure complete dissolution of the starting material. The sol–gel technique used consists of preparing

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*Corresponding author. Fax: +55-1-3816-9343.

E-mail address: enavarro@usp.br (E.N.S. Muccillo).

a mixed solution of the desired cations and adding to it another solution containing a complexant agent. Citric acid (monohydrated–mw=210.14 g mol^{-1}) was used for this purpose. The molar ratio citric acid:[Zr+Nd]:[H$_2$O] was set to 17.5:1:300. This molar ratio was used previously for the preparation of ceria and yttria doped zirconia ceramics [10]. The mixed solution was heated to 140 °C for ~3 h under stirring to remove excess water and to convert it to a transparent gel. While raising the temperature, the solution became more viscous with evolution of foam, and finally it gelled without any visible formation of precipitation or turbidity. Maintaining the solution at this temperature, there is an increase of the viscosity with simultaneous elimination of water and NO$_2$, resulting in a white resin. This resin was partially decomposed at 250 °C. Total thermal decomposition was carried out at 700 °C/1 h according to results obtained by thermal analyses.

Thermogravimetric and differential thermal analyses (STA 409, Netzsch) were carried out to follow the decomposition of the resin. Alumina was used as reference material. Specimens were heated at 5 °C/min to 1200 °C and cooled at 10 °C/min under dynamic synthetic air. X-ray diffraction experiments (D8 Advance, Bruker-AXS) were performed on calcined powders and sintered specimens for phase identification and crystallite size determination. The crystallite size (d_{XRD}) of the calcined powder was estimated using the Scherrer equation $d_{XRD}=0.94\lambda/(\beta \cos \theta)$, where λ is the wavelength of the X-ray and θ is the scattering angle of the main reflection [11]. Silicon powder was used as standard for this measurement. The particle size distribution was measured by laser scattering (1064, Cilas). The morphology of the calcined powder was observed in a scanning electron microscope (XL30, Philips). The linear shrinkage of a powder compact was measured up to 1650 °C at a heating rate of 8 °C/min in a dilatometer (DIL 402 E/7, Netzsch).

3. Results and discussion

Results obtained for the solid solution containing 5 mol% Nd$_2$O$_3$ will be shown; unless mentioned in the text, similar results were obtained for other compositions.

The thermal decomposition of resins resulted in a fine powder with a pale violet color characteristic of neodymium ion. Typical TG–DTA curves are shown in Fig. 1. Endothermic peaks below ~200 °C are related to dehydration and evaporation of water. In the temperature range of 200–700 °C, exothermic peaks are observed. These peaks are related to the burn out of organic materials and to the crystallization reaction. In previous works [12–15] using this technique to prepare other ceramic compositions, the exothermic evolutions have been assigned to the liberation of NO$_2$, CO, CO$_2$ and H$_2$O as major components. The TG curve of the resin shows that the total weight loss up to ~500 °C is 90.6%. Most of this weight
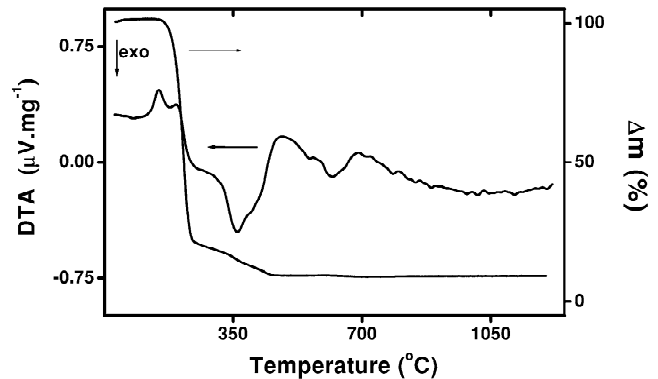

Fig. 1. Thermogravimetric and differential thermal analysis curves of the resin.

loss (78%) occurs up to 240 °C. A second step of weight loss (12.6%) is observed between 240 and 500 °C, and for higher temperatures the weight loss is negligible.

Fig. 2 shows the particle size distribution curve of the powder after thermal decomposition at 700 °C. The maximum particle size is ~20 μm. From the 50% cumulative mass, an average particle size of 3 μm is obtained. However, the distribution is irregular showing that it might be related to agglomerated particles. Another important feature of the sol–gel technique employed here is that the distribution of particle sizes is sharp (as most of particles/agglomerates lie below 20 μm) when compared to those usually obtained for solid solutions prepared by the conventional technique of powder mixing.

The morphology of particles/agglomerates is shown in the scanning electron microscopy micrograph of Fig. 3. This micrograph shows that an ultrafine powder has been obtained by the sol–gel technique and that particles are in the form of round agglomerates.

The linear shrinkage of a powder compact is shown in Fig. 4. The total shrinkage reaches close to 30% and the rate of retraction is higher in the temperature range between 1100 and 1500 °C. During cooling a small expan-
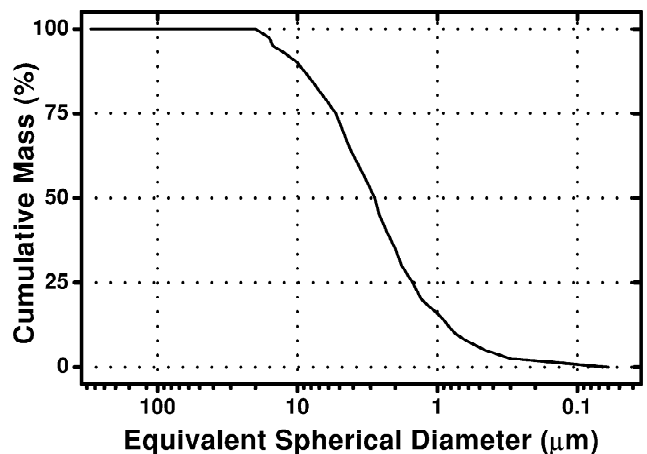

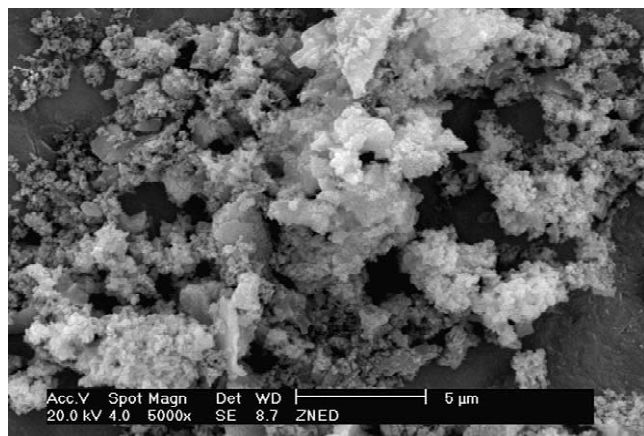Fig. 2. Distribution of particle size in the calcined powder.

Fig. 3. Scanning electron microscopy micrograph of the calcined powder.

Fig. 5. X-ray diffraction patterns of calcined (700 °C / 1 h) powder (a) and sintered (1500 °C / 1 h) pellets. Specimens composition: 8 (a,b), 5 (c) and 3 mol% neodymia (d).

sion around 750 °C is observed. This expansion is related to the tetragonal to monoclinic and pyrochlore structures phase transformation. This phase transformation was observed to occur at approximately 880 °C in solid solutions prepared by a chemical method [3]. This reduction in the temperature for phase transformation can be attributed to different temperatures of thermal treatments and to the higher shrinkage obtained in this study. It is generally known that the tetragonal phase stability in zirconia matrices is also a function of particle constraint [16].

Fig. 5 shows XRD patterns of the ZrO_2–Nd_2O_3 calcined powder (Fig. 5a) and sintered pellets (Fig. 5b–d). The powder pattern, obtained for the 8 mol% Nd_2O_3 solid solution composition, exhibits the main reflections due to the tetragonal phase. The crystallite size estimated assuming a Gaussian shape for the (111) peak is 5.0 nm. Peaks of the tetragonal, monoclinic and pyrochlore phases are clearly observed in the diffraction pattern of sintered specimens. This shows that the total stabilization of the cubic solid solution occurs for higher concentrations of neodymium, in contrast to the zirconia–yttria solid solution. For specimens containing 5 (Fig. 5c) and 3 mol%
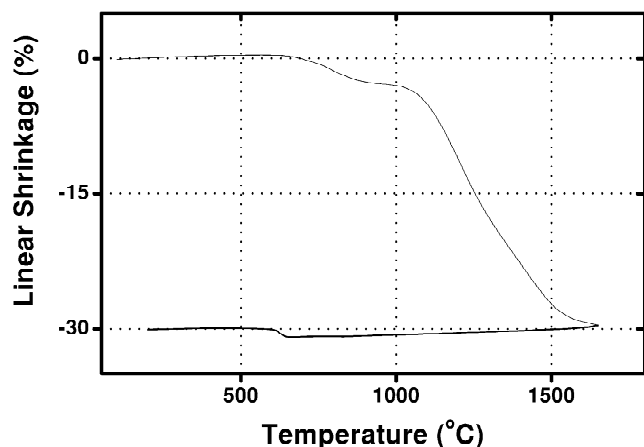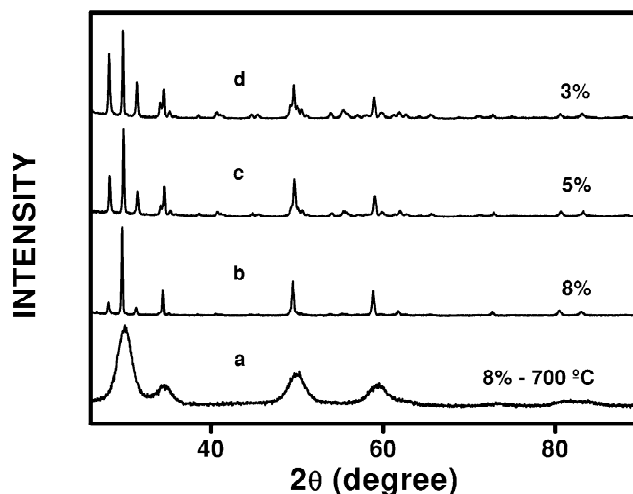
Nd_2O_3 (Fig. 5d), the XRD patterns are quite similar except for the relative concentrations of monoclinic and pyrochlore phases, that are observed to increase with decreasing neodymia content.

4. Conclusions

Ultrafine particles of neodymia-doped zirconia solid solutions have been prepared by the sol–gel technique. Total decomposition of the precursors was obtained at 700 °C. The particle size distribution is relatively sharp. The morphology of calcined powders is characterized by agglomerated nanosized particles. The linear shrinkage of a powder compact reaches 30% up to 1650 °C. XRD patterns are consistent with the tetragonal to monoclinic and pyrochlore phase transformation. The main advantages of this synthesis technique in comparison with coprecipitation or conventional routes are the relative simplicity, low cost, and effectiveness for obtaining reactive ceramic powders.

Acknowledgements

Fig. 4. Linear shrinkage curve of a powder compact.

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