Powder Technology 228 (2012) 272–276

Contents lists available at SciVerse ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Characterization of agglomeration state in nanocrystalline 3YSZ powders through pressure–displacement curves and nanoindentation of green compacts

Sharanabasappa B. Patil, Parag Bhargava *

Department of Metallurgical Engineering and Materials Science, IIT Bombay Powai Mumbai 400076, India

ARTICLE INFO

Article history:
Received 28 December 2011
Received in revised form 9 May 2012
Accepted 12 May 2012
Available online 19 May 2012

Keywords:
Yttria-stabilized zirconia
Agglomeration
Temperatures
Powders
Green compacts
Density

ABSTRACT

Nanocrystalline 3YSZ (3 mol% yttria stabilized zirconia) powders were synthesized through co-precipitation followed by washing with ethanol and calcination at different temperatures in the range of 470–900 °C. The powders calcined at different temperatures showed apparent differences in the state of agglomeration. Besides the use of conventional techniques, such as Transmission Electron Microscope (TEM), for observation of crystallite size and agglomeration in powders, the differences in state of agglomeration of the powders were examined through pressure–displacement behavior during powder compaction, nanoindentation of green powder compacts. The observations from load–displacement behavior were shown to be correlated to resistance to penetration of green compacts during nanoindentation as well as the green and sintered densities.

1. Introduction

The growing importance of yttria-stabilized zirconia as an advanced ceramic material is due to its superior mechanical properties and high ionic conductivity. 3 mol% yttria stabilized zirconia(3YSZ) due to its high fracture toughness and chemical stability has also proven to be a suitable material for dental application, industrial cutters and milling media [1,2]. The fracture toughness of 3YSZ (tetragonal zirconia) can be enhanced with fine grains (<500 nm) in highly densified bodies [3,4]. To achieve this, the starting powders must be comprised of weakly agglomerated nanocrystalline particles. Over the years many approaches have been developed for synthesis of partially or fully stabilized nanocrystalline zirconia powders but controlling the state of agglomeration in nanocrystalline powders has remained a challenge [5–29]. The extent of agglomeration in nanoceramic materials has been found to be dependent on synthesis route including the temperature of calcination of amorphous intermediates which results in crystallization [5]. Hydrothermal synthesis typically does not involve high temperature calcination and thus results in lower extent of agglomeration of particles [16–21]. Wet chemical route for synthesis of nanoparticles have gained more attention due to possibility of control over starting precursor solutions and intermediates formed during the process of synthesis [5,6]. Among the available wet synthesis routes, coprecipitation technique appears to be attractive due to its ability to produce powders at large scale and low cost investment.

During preliminary work carried out by the present authors it was observed that the powders produced by coprecipitation resulted in agglomerated powders, which hardly showed any densification after sintering. It has been reported in literature [7–10] that during drying of the coprecipitated mass, high surface tension of water (73 mN/m) is responsible for bringing the zirconium hydroxide nanoparticles closer resulting into hard agglomerates. On treating the water washed precipitate with ethanol the extent of agglomeration reduces considerably because of low surface tension of ethanol(24 mN/m). On drying, ethanol washed particles remain separated due to absence of hydroxyl bridging between particles which leads to reduced degree of agglomeration. Also, it has been reported [6,15–17] that washing of water washed coprecipitated mass of yttrium-zirconium hydroxide with solvents such as methanol, butanol and propanol reduces the extent of agglomeration. In addition to the washing medium, drying temperature also significantly influences the deagglomeration state of YSZ powders [23]. Heuer et. al.[8] reported that after washing the precipitate with ethanol for several times followed by drying at 110 °C and calcination at temperatures such as 400 °C, 600 °C and 800 °C the powder retains its deagglomerated state with increased particle size. The work by Heuer et.al. [8] mainly reported compaction and sintering behavior of powders calcined at 800 °C. While a low calcination temperature may be preferred to retain fine crystallite/particle size to have high sinterability, finer crystallite/particle size result in greater agglomeration making it more difficult to produce dense sintered compacts. Higher temperature calcination may provide powder particles that are less agglomerated due to coarsening of particles and yet have reasonable sinterability. The present study has been undertaken to examine the influence of calcination temperatures on agglomeration

* Corresponding author.
E-mail address: pbhargava@iitb.ac.in (P. Bhargava).

0032-5910/$ – see front matter © 2012 Published by Elsevier B.V.
doi:10.1016/j.powtec.2012.05.030

state of nanopowders through study of powder compaction and characterization of green compacts.

2. Experimental work

2.1. Materials used

The starting materials used in the present study were zirconium oxychloride ($ZrOCl_2.8H_2O$) (Zirconium Chemicals Private Limited, Mumbai, India) of 99% purity (Remaining 1% accounts for the presence of Fe, Na, Ti, Ca) and yttrium oxide (Y_2O_3 99.99% AR Grade) (Spectrochem Pvt. Ltd., India), double distilled water(0.7 μS/cm), nitric acid (35% Conc. Thomas Baker, India), ammonia (25% Conc. Thomas Baker India) and absolute ethanol.

2.2. Synthesis

Synthesis of 3mole% yttria stabilized zirconia was carried out by reverse-strike coprecipitation method followed by drying and calcination of the coprecipitated mass at high temperatures i.e., 470 °C to 900 °C. Precursor solutions of 0.5 M zirconium oxychloride were prepared in double distilled water using magnetic stirrer. Yttrium nitrate solution was prepared by adding Y_2O_3 in stirred mixture of double distilled water and nitric acid (1:1 ratio). Zirconium and yttrium containing precursor solution were prepared by adding appropriate amount of yttrium nitrate solution to zirconium oxychloride solution to achieve 3 mol% yttria with zirconia in the calcined mass. The prepared precursor solution was added drop wise into a continuously stirred ammonia solution ensuring the pH remained above 11 till complete addition of precursor solution to ammonia. Stirring was continued for 2 h after complete addition of precursor solution into ammonia. The precipitate was left overnight to settle (~12 h) and then filtered on fabric cloth for the removal of excess ammonia. This precipitate was washed with distilled water till Cl^- ion was completely removed from the precipitate. The absence of Cl^- ion was confirmed by absence of AgCl precipitate up on addition of 0.1 N $AgNO_3$ solution in the filtrate. Water washed precipitate was treated with ethanol (1:2.5; water of precipitate to ethanol ratio) and quantity of ethanol was chosen in reference to the quantity of water present in the precipitate. Water associated with the washed and filtered coprecipitated mass was determined by drying known quantity of coprecipitated mass at 100 °C. This amount of water in precipitate was reproducibly seen to be around 93% of the filtered coprecipitated mass. The precipitate was washed with ethanol twice followed by drying at 100 °C. The dried precipitate was calcined at 470 °C, 600 °C, 700 °C, 800 °C and 900 °C separately and soaking time of 120 min was maintained for each of the calcination temperature. In the remaining text zirconium hydroxide precipitate refers to the precipitate with composition expected to yield crystalline 3 mol% yttria stabilized zirconia (3YSZ) upon calcination.

2.3. Characterization

The powders calcined at 470 °C were subjected to x-ray diffraction (XRD) for phase analysis (40 kV, 30 mA, Panalytical Expert Pro, Netherlands) and Confocal micro-Raman Spectrometer (Labram HR800, TI900, Hystron Inc., USA) for confirmation of phase content. The powders that were calcined at different temperature were characterized with transmission electron microscope (FEG-TEM, 200 kV, JEOL Japan) to observe particle size, morphology and agglomeration state.

To understand the state of agglomeration through study of compaction behavior of 3YSZ nanocrystalline powder a universal mechanical testing machine (UTM) (H25KS-UTM, Tinius Olsen Ltd., UK) was used. Load cell of 25000 Newtons capacity and a hardened steel die of 6 mm diameter (internal cavity) were used for the compaction experiments. Stearic acid was used as a die lubricant to minimize powder-die frictional forces during powder compaction. A fixed amount of powder (300 mg) was used for each of the compaction experiments. Pressure–displacement curves for powder compaction were obtained up to the maximum load of 200 MPa (5800 Newtons) and cross head displacement speed of 1 mm/min was maintained for all compaction experiments. The displacement was measured by the rate of movement of the crosshead which pushed the top punch to achieve compaction of powders. The pressure (axial stress) was calculated from the load registered by the load cell during powder compaction and the cross-section area of the die. These compacted samples were subjected to nanointendation (TriboIntender TI900, Hystron Inc., USA) to characterize particle packing in green compacts. For each of the samples, indentation was made at three different regions.

All the powders that were calcined at different temperatures were compacted uniaxially at 200 MPa, sintered at 1400 °C for 30 min and soaked at 1200 °C for 2 h. Densities of the sintered samples were measured by Archimedes principle and microstructural features were observed under FEG-SEM(7200S JEOL, Japan).

3. Results and discussion

All the 3YSZ samples prepared in the present study were predominantly tetragonal as evident from XRD pattern and Raman spectroscopy shown in Figs. 1 and 2 respectively. The peaks at 260 cm^{-1} and 464 cm^{-1} in the Raman spectra were attributed to the presence of tetragonal phase, as reported in the literature [30,31]. Absence of peaks in the range of 170 cm^{-1} to 189 cm^{-1} (monoclinic peaks) proved that tetragonal is the major phase in the synthesized powder. All the YSZ powders in this study were produced by calcination of ethanol washed coprecipitated mass. Reports in the literature have already pointed out the significance of washing of the precipitate with ethanol in producing deagglomerated calcined powders. [7–11].

The particle size and its distribution in all the calcined powders were observed through TEM micrographs shown in Fig. 3. It can be seen from TEM images that particle size increased with increase in calcination temperature, as expected.

Usually, compaction curves (pressure vs compact density) are used to examine compressibility of powders, deformation of granules, particle rearrangement and evolution of powder packing [16,25–27,32–34]. In the present study powder compaction in terms of pressure (axial stress) versus punch displacement has been used to examine the agglomeration state of the 3YSZ nanopowders produced by calcination of the coprecipitated mass at different temperatures. Fig. 4 shows the pressure–punch displacement curves for all the powders. It must be

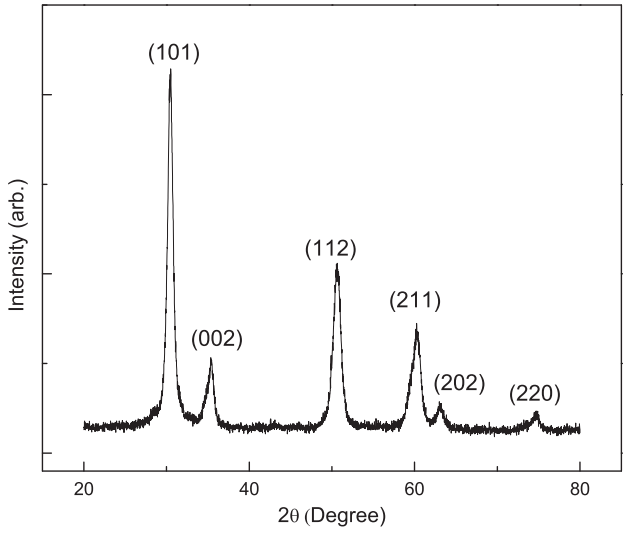

Fig. 1. A representative XRD pattern for 3YSZ nanocrystalline powders wherein the precipitate was washed with ethanol and calcined at 470 °C.