Journal of the European Ceramic Society xxx (2016) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

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

Feature article

Densification and grain growth of $Gd_2Zr_2O_7$ nanoceramics during pressureless sintering

Mao Zhou[a,b], Zhangyi Huang[a,b], Jianqi Qi[a,b,*], Nian Wei[a,c], Di Wu[d], Qinghua Zhang[a,b], Shanshan Wang[a,b], Zhao Feng[a,b], Tiecheng Lu[a,b,c,*]

[a] College of Physical Science and Technology, Sichuan University, Chengdu 610064, China
[b] Key Laboratory of Radiation Physics and Technology of Ministry of Education, Sichuan University, Chengdu 610064, China
[c] Key Laboratory of High Energy Density Physics of Ministry of Education, Sichuan University, Chengdu 610064, China
[d] The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99163, United States

ARTICLE INFO

Article history:
Received 16 July 2016
Received in revised form
19 September 2016
Accepted 19 September 2016
Available online xxx

Keywords:
$Gd_2Zr_2O_7$ nanoceramics
Pressureless method
Densification behavior
Two-step sintering

ABSTRACT

$Gd_2Zr_2O_7$ nanoceramics were fabricated using pressureless sintering method, in which the nanopowders were synthesized via solvothermal approach. The effects of starting powders on grain growth and densification during sintering of ceramics were revealed. Two distinct pressureless sintering methods were investigated, including conventional and two-step sintering. The sample grain size increases abruptly as sintering temperature increases during conventional sintering. In contrast, in two-step sintering, abnormal or discontinuous grain growth was suppressed in the second step, leading to $Gd_2Zr_2O_7$ nanoceramics formation (average grain size 83 nm, relative density ~93%). Such distinct behaviors may originate from the interplay between kinetic factors such as grain boundary migration and diffusion. Moreover, suppression of grain growth and promotion of densification in the two-step sintering are mainly due to dominant role of grain boundary diffusion during the second-step sintering process.

1. Introduction

Substantial efforts have been made to design and optimize sintering strategies to achieve accurately controlled grain growth and densification in fabrication of nanoceramics [1]. Nanoceramics have many advantages, such as low energy, minimized residual porosity and reduced crystallographic thermal expansion owing to decreased firing temperature [2].

Typically, the nanoparticles in ceramics have high surface energy, which may alter its structure and morphology, for example, stabilizing a metastable phase [3]. However, fabrication of dense bulk nanocrystalline ceramics is very challenging, since to make high-density ceramics high sintering temperature is necessary, which usually leads to inevitable grain coarsening. In contrast, sintering at lower temperature can only produce materials with smaller grain size. High-density is usually sacrificed [4]. Moreover, the sintered density is very sensitive to even slight sintering temperature variation [5]. At high temperature, single grain can grow rapidly by consuming a large numbers of surrounding grains, in which smaller grains dissolve and feed crystal growth of larger particles [6,7]. Notably, closed pores are mostly isolated from grain boundaries as a result of discontinuous grain growth [8]. Fine grain size and full densification are two competing factors of the most importance for nanoceramic fabrication [9].

Owing to its promising applications for nuclear waste disposal and thermophysical properties, numerous studies have been performed on $Gd_2Zr_2O_7$ [10,11]. Although it has potential to be employed as thermal barrier coating material, the relatively poor fracturing toughness limits its application [12]. Ceramics with nano-sized grains can overcome these drawbacks [13]. Sintering methods such as spark plasma and microwave sintering [14–16] were employed to sinter $Gd_2Zr_2O_7$ nanoceramics with improved properties. Xu et al. [16] obtained ceramics with a 92% final density and a grain size of 20 μm using microwave sintering of $Gd_2Zr_2O_7$ compacts, while abnormal grain growth were observed. However, spark plasma sintering has several intrinsic disadvantages. First, it is difficult to analyze the diffusion mechanism and trace the exact sintering process. In addition, this technique also requires expensive equipment setup, which is not cost effective [1].

Using microwave sintering, Lu et al. sintered ceramics with small grain size (2.4 μm) and high density [17]. Nevertheless, it was difficult to monitor and control sintering temperature in

* Corresponding authors at: College of Physical Science and Technology, Sichuan University, Chengdu 610064, China.
E-mail addresses: qijianqi@scu.edu.cn, qijianqi@gmail.com (J. Qi), lutiecheng@scu.edu.cn (T. Lu).

http://dx.doi.org/10.1016/j.jeurceramsoc.2016.09.019
0955-2219/

Table 1
Conditions of preparing green pellets.

Samples	Calcination temperature of starting powders (°C)	Pressure (MPa)	ρ (g/cm^3)	ρ (%)
1	800	10	3.59 ± 0.13	52.0 ± 1.88
2	900	10	3.95 ± 0.17	57.2 ± 2.46
3	1000	10	4.57 ± 0.11	66.2 ± 1.59
4	1100	10	4.19 ± 0.19	60.7 ± 2.75
5	1200	10	3.71 ± 0.09	53.8 ± 1.30

Table 2
Summary of Two-Step sintering conditions.

Conditions	TEMP1 (°C)	Time1 (h)	TEMP2 (°C)	Time2 (h)
TSS1	1350	1	1213	10
TSS1	1382	1	1213	10
TSS1	1450	1	1213	10
TSS2	1350	1	1213	20
TSS2	1382	1	1213	20
TSS3	1250	1	1100	20
TSS3	1382	1	1100	20

microwave sintering, which may cause excessive grain growth due to liquid phase formation [1]. Chen and Wang [18] developed an effective approach, two-step sintering (TSS), for Y_2O_3 fabrication, which obtained fully dense nanoceramics by fine-tuning the "kinetic window" between grain boundary diffusion and grain boundary migration. However, $Gd_2Zr_2O_7$ ceramics fabricated with nanoparticles by pressureless sintering has not been previously reported.

Herein, we report a simple and cost-effective pressureless method containing a two-step temperature schedule to manufacture $Gd_2Zr_2O_7$ nanoceramics with high density. The ceramic samples were fully characterized. The fabrication process was analyzed and compared with the conventional, one-step sintering method. Specifically, we interpreted the conventional sintering process, in which the nanoceramics were sintered at various temperatures. The temperature effects on grain growth behaviors and densification mechanisms were analyzed and discussed. For the $Gd_2Zr_2O_7$ nanoceramics system, the size of nanoscale grains of starting powders plays an important role. On the other hand, in the two-step sintering, the sintering temperature in the first step follows the behavior of conventional sintering. Moreover, several different TSS programs were designed to study the effect of sintering temperature, holding time and the grain size of the starting powder on the formation of $Gd_2Zr_2O_7$ ceramics, especially, its relative density and the grain growth.

2. Experimental procedure

Solvothermal method was used in sample preparation. Specifically, the starting materials, $Gd(NO_3)_3{\cdot}6H_2O$ (>99.99%, Aladdin) and $ZrOCl_2{\cdot}8H_2O$ (>99.99%, Aladdin), were mixed according to the appropriate molar ratios of 1:1 and dissolved in deionized water with a concentration of 0.03 mol/L (Gd^{3+} and Zr^{4+}). This mixture was pumped into diluted ammonium hydroxide until the pH reached 10.3. The gelling product was filtered and washed for two rounds, with deionized water (first round) and ethyl alcohol (second round). Then, this homogeneous mixture dissolved in ethanol was introduced into a stainless-steel autoclave and kept at 200 °C for 24 h. The precipitates (precursors) were washed with ethanol and dried for dehydration to obtain the final powders, which were further sieved and calcinated at 500 °C for 2 h to produce the starting $Gd_2Zr_2O_7$ powders. In addition, to investigate the grain growth and densification of nanoceramics as the crystal size of powders varies, we calcinated the starting $Gd_2Zr_2O_7$ powders at a series of temperature, ranging from 800 °C to 1200 °C.

The green pellets, 7 mm in diameter and 2–3 mm in thickness, were obtained by uniaxial pressing of the calcinated nanopowders with various particle sizes (see Table 1), which were heated to 1250 °C at 5 °C/min and sintered for 10 h to fabricate the $Gd_2Zr_2O_7$ ceramics. In the conventional pressureless sintering method, a series of sintering temperatures ranging from 1250 to 1500 °C (holding 1 h) were applied. On the other hand, to fabricate nanoceramics with higher density, a two-step sintering approach (TSS, see Table 2) was introduced in the present study. Typically, in the TSS method, each sample was heated to a high temperature (T_1) at 5 °C/min, held for 5 min to 1 h. Subsequently, it was cooled down to a lower temperature (T_2) at 8 °C/min dwelling for 10–20 h.

The green density and the final densities of the sintered compacts were determined by the Archimedes method with kerosene and deionized water as immersion medium respectively, using the value 6.90 g/cm^3 as the theoretical density for all the samples. The phases (crystal structures) of all samples were examined by powder X-ray diffraction (XRD, Model DX-2700, Dandong Fangyuan Instrument Co, Ltd, Liaoning, China). Transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN, FEI, Hillsboro, OR) images were collected to analyze the microstructure and morphology of all powder samples. The microstructure of ceramics was monitored and analyzed by scanning electron microscopy (SEM, Model S-4800, Hitachi, Japan). The mean particle size of calcinated powders and the average grain size of bulk ceramics were determined by XRD data using Scherrer equation and also directly measured from the SEM images. Prior to SEM experiments, the samples were polished and thermally etched in air for 2 h at a temperature 200 °C below the sintering temperature.

3. Results and discussion

3.1. Characteristics of powders

The microstructure of $Gd_2Zr_2O_7$ nanopowders is presented in Fig. 1. According to the TEM images, the starting powders calcined at 500 °C are composed of spherical particles with homogeneous size distribution. The mean particle size of the powder is 4 nm, which is consistent with the average grain size calculated from XRD data. The XRD patterns of the starting nanopowders calcinated at different temperatures, from 800 to 1200 °C (2 h) are shown in Fig. 2(a). All samples appear to be metastable fluorite phase. As calcination temperature increases clear diffraction peak narrowing is observed. This suggests that the grain size (crystallite growth) of nanopowders is a function of calcination temperature. The grain sizes can be derived quantitatively from the XRD data using Scherrer equation. Specifically, the grain sizes are confirmed to be nano-sized, ranging from 4 to 40 nm (see plot in Fig. 2(b)).

3.2. Conventional sintering

The relative density (%) and grain size (nm) of ceramics are plotted in Fig. 3 as a function of calcination temperature applied on the starting powders. Since all ceramics were sintered in air at 1250 °C with a soaking time about 10 h, the general trends of plot a and b in Fig. 3 reflect the effect of calcination temperature on relative density and grain size. Generally, higher temperature can provide sufficient driving force resulting in ceramics with higher density. At relatively low temperature, the relative density of sintered $Gd_2Zr_2O_7$ nanoceramics increases as the grain size of powders increases. Interestingly, the relative density reaches a maximum (80%) at about 1000 °C (see plot in Fig. 3). The corresponding ceramic microstructure of this maximum point is shown in Fig. 4(c). Further calcination temperature increase beyond 1000 °C leads to relative density of ceramics depression from 80 to 75%. In con-

Please cite this article in press as: M. Zhou, et al., Densification and grain growth of $Gd_2Zr_2O_7$ nanoceramics during pressureless sintering, *J Eur Ceram Soc* (2016), http://dx.doi.org/10.1016/j.jeurceramsoc.2016.09.019