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Two-step sintering of nanocrystalline $8Y_2O_3$ stabilized ZrO_2 synthesized by glycine nitrate process

Mehdi Mazaheri, M. Valefi, Z. Razavi Hesabi, S.K. Sadrnezhaad *

Materials and Energy Research Center, P.O. Box 14155-4777, Tehran, Iran

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Abstract

Two-step sintering was employed to consolidate nanocrystalline 8 mol% yittria stabilized zirconia processed by glycine-nitrate method. Results verified the applicability of this method to suppress the final stage of grain growth in the system. The grain size of the high density compacts (>97%) produced by two-step sintering method was seven times less than the pieces made by the conventional sintering technique. Up to ~96% increase in the fracture toughness was observed (i.e. from 1.61 to 3.16 MPa $m^{1/2}$) with decreasing of the grain size from ~2.15 to ~295 nm. A better densification behavior was also observed at higher compacting pressures.

Keywords: 8Y-FSZ; Two-step sintering; Nanocrystalline; Fracture toughness

1. Introduction

Interest in synthesis and sintering of nanocrystalline ceramics have recently grown due to the significant improvement in their properties as compared to the conventional coarser grain compacts. There are many methods for preparation of nanocrystalline powders. Examples are sol–gel [1], chemical vapor synthesis (CVS) [2,3], combustion synthesis [4] and hydrothermal processing [5]. Among different routes, combustion synthesis is known as the most energy efficient, low cost and high yield technique capable of producing single or multi component high-purity oxides [4].

Yittria stabilized cubic zirconia (YCSZ) possesses high oxygen ionic conductivity and chemical stability over a wide range of temperature and oxygen partial pressure. It is, therefore, a well-known candidate for applications such as manufacturing of oxygen sensor, development of solid oxide fuel cell and making membrane for separation of oxygen [6–10]. In contrast to the tetragonal zirconia, low fracture toughness restricts the use of cubic zirconia as an electrolyte because of premature fracture due to the thermal and mechanical stresses [11–13]. Grain refining is a promising route for simultaneous increase of mechanical strength and fracture toughness [14]. The decrease of the grain size below 100 nm leads to the formation of attractive nanostructured ceramics having superior electrical [7,15], thermal [16], optical [17] and mechanical properties [18]. In addition to these advantages, using nanopowder to fabricate nanocrystalline parts considerably enhances sinterability at lower temperatures rather than those of micrometric grains. An accelerated grain growth during densification of nanopowder is, however, reported deteriorating the advantages of nanostructured bulk materials [19]. Spark plasma sintering and hot pressing are two promising techniques for production of nanostructured ceramics [20,21]. Equipments of these methods are, however, too sophisticated and unavailable as well as very expensive. To fabricate nanocrystalline ceramics by pressure-less conventional sintering route, grain boundary migration has to be abated. The grain growth in this process can be controlled by two approaches: one is to prohibit grain growth by addition or dispersion of a second phase particles; the other is to control grain growth by a novel processing method called two-step sintering (TSS) technique.

Tekeli et al. [22–24] added Al_2O_3 and SiO_2 particles to hamper grain growth in cubic phase zirconia. They showed that the dispersion of a small amount ($\leq$1 wt%) of second phase can improve the densification and suppress the grain growth. With

* Corresponding author. Fax: +98 21 88773352.
E-mail addresses: mmazaheri@gmail.com (M. Mazaheri), sadrnezh@sharif.edu (S.K. Sadrnezhaad).

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increasing of the amount of the second phase, the densification would be degraded while the final grain size would be significantly decreased [13]. It was attributed to the formation of porosities located in the grain interior and along the grain boundaries. Another problem of using second phase particles was that the homogenous distribution of second phase grains in the matrix was extremely difficult. This could probably decrease the sintering rate by inducing tensile mean-stress developed by differential shrinkage characteristics between second phase particles and matrix grains [22]. Zirconia grains around the perimeter of the second phase particles were unable to contact with each other freely. This was another reason for decreasing of the sintering rate.

Chen et al. [25] and Lei and Zhu [26] added TiO_2 and Sc_2O_3, respectively. Though the grain growth can be hindered by the addition of dopants such as SiO_2, Al_2O_3 and SiC, insulating phases can also be formed. These phases can cause degradation of ionic conductivity [25]. Han et al. [7] have reported that as the YSZ grain size becomes smaller the thickness of the intergranular region decreases, too. Consequently, intergranular conductivity would increase. An enhancement of 1–2 orders of magnitude in the specific grain boundary conductivity for YSZ was observed after the grain size of solid electrolyte reduced to nanocrystalline range [27]. While the second phase particles were added to control grain size, these particles located at grain boundaries resulting in increasing of the grain boundary width deteriorating grain boundary conductivity. Seemingly, the addition of second phase causes technical problems for fabrication of uniform, dense and ultrafine structure without degradation of ionic conductivity.

Another way to control grain growth uses novel processing technique to tailor the microstructure. Recently, a two-step sintering method has been proposed to achieve the densification of ceramic bodies without significant grain growth in the final stage of sintering [28]. This method modifies the sintering regimes by high temperature firing followed by rapid cooling and low temperature soaking of the samples. To succeed in two-step sintering, a sufficiently high starting density should be obtained during the first step. When the density is greater than a critical value, the pores become subcritical and unstable against shrinkage which is induced by capillary action. These pores can be filled as long as grain boundary diffusion allows, even if the particle network is frozen as it is clearly in the second step. Mazaheri et al. [29] have suggested proper temperatures for first (T_1) and second stages (T_2) in two-step sintering to prohibit grain growth without degradation of densification. On the contrary, the inappropriate regime can serve no evolution in densification as well as no remarkable grain growth difference in comparison with normal sintering (NS) [29].

Han et al. [7] used TSS technique to control the grain growth of YSZ nanopowder synthesized by a liquid phase method. Laberty-Robert et al. [8] as well as Ghosh et al. [30] have also investigated the effect of two-step sintering on microstructure of yittria stabilized zirconia. Yu et al. [31] took the benefit of this technique for sintering of powder injection-molded zirconia parts.

In addition to 8YSZ, two-step sintering has been successfully conducted on ZnO [29], Ni–Cu–Zn ferrite [32], $BaTiO_3$ [32], Al_2O_3 [33,34] and liquid phase sintering of SiC [35] as well as doped ZnO varistors [36].

In this study, two-step sintering is applied on nanocrystalline 8YSZ synthesized by glycine-nitrate process to achieve a dense ultrafine structure. The sintering behavior and microstructural evolution during densification of normal and two-step sintering process are compared. A comparison is also made of the mechanical properties of the ceramic bodies made by TSS technique with those of the normally sintered ones.

2. Experimental procedure

Experiments consisted of synthesis, characterization, compaction, sintering and mechanical properties determination of 8YSZ samples according to the following methods.

2.1. Powder synthesis and characterization

Nanocrystalline 8 mol% yittria stabilized zirconia was synthesized via glycine-nitrate process in a muffle furnace using zirconyl nitrate ($ZrO(NO_3)_2{\cdot}6H_2O$) and yttrium nitrate ($Y(NO_3)_3{\cdot}6H_2O$) as sources of oxidants with the elemental stoichiometric coefficient $\Phi = 1.163$. Details of the processing method and the characteristics of as-synthesized particles were the same as those reported in Ref. [4].

In order to break the foamy agglomerates, the as-synthesized sheet-like nanocrystalline agglomerates were milled in a planetary ball mill. The milling was conducted in isopropanol medium using zirconia balls at rotational speed of 200 rpm. The milled powder was dried in air at 60 °C for 24 h. The morphology of the powder was investigated by scanning electron microscopy (Philips XL30, Netherlands) and transmission electron microscopy (Philips CM 200 FEG, Netherlands). The specific surface area of the powder was determined by Brunauer–Emmett–Teller (BET) technique (Micromeretics Gemini 2375, USA).

2.2. Compaction

The compressibility curve of the powder was determined by pressing the powder in a steel cylindrical die (10 mm diameter). The milled powder was uniaxially pressed at different pressures. After ejection of the compacts from the die, the green density of the pellets was measured by volumetric method. This method consisted of measuring weight and dimensions of the compacts by using an accurate balance (10^{-5} g) and a micrometer caliper (10^{-5} m).

2.3. Sintering

The green bodies were non-isothermally sintered with a heating rate of (1/12) °C s^{-1} up to 1500 °C without holding at the highest temperature. Two-step sintering was conducted on samples pressed at 600 MPa with relative density of about 48.5% with respect to the theoretical density (TD). At the first