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Controlled amorphous crystallization: An easy way to make transparent nanoceramics

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ABSTRACT

Fabrication of transparent nanoceramics is attracting more and more interests recently. In this study a new method of amorphous sintering followed by controlled crystallization (ASCC) was developed, and transparent $LaAlO_3$/t-ZrO_2 nanoceramic was prepared as an example. Based on a eutectic composition of Al_2O_3–La_2O_3–ZrO_2, glass powders were synthesized, sintered, and then converted to nanoceramics by post-heat-treatment. The heat-treatment performed at 1200 °C for 2 h produced a transparent $LaAlO_3$/t-ZrO_2 nanoceramic with an average grain size of 40 nm. Due to the nanoscale microstructure, the ceramic showed a transparency up to 55% at 800 nm (1 mm thick), Vickers hardness of 19.05 GPa, and fracture toughness of 2.64 MPa $m^{1/2}$, respectively.

1. Introduction

Transparent ceramics are receiving wide attentions because of their important applications in high-performance laser hosts instead of single crystals [1–4]. Many works have been done to tailor the microstructure, e.g. the elimination of pores and refinement of grain size, in order to reduce light scattering and increase laser excitation efficiency. It is generally considered that pore-free nanoceramics are promising to achieve excellent combination properties [1,4].

Recently, encouraging advances in optical performance of transparent ceramics in non-cubic system caused by the refinement of grain size have been reported. For example, the in-line transmittance of Al_2O_3 ceramic greatly increases when the grain size is reduced into submicron scale, which makes translucent sample become transparent [5]. This indicates that the optical properties of the non-cubic ceramics are intensively dependent on the grain size because of their high anisotropic lattice (for α-Al_2O_3, $c/a = 2.72$) [6]. Based on the Rayleigh–Gans–Debye light-scattering theory, Apetz et al. developed a model to describe the light transmission characteristics of fine-grained non-cubic ceramics [7]. This model explains the noteworthy transparency of the submicron-grained α-Al_2O_3 ceramic, and suggests that the light transmission will remarkably increase with the reduction of grain size. That is, if the grain size can further be reduced to nano-scale, the light transmission of transparent ceramic will be greatly improved.

While in conventional sintering of ceramic powders, the high temperature required for densification would promote extensive grain growth, which makes it very difficult to prepare fully-dense nanoceramics [8]. Therefore, three main methods have peen proposed to prevent grain growth during sintering: application of hot-pressing or sintering forging under high pressure low temperature, addition of dopant to modify diffusion process, and sintering powders in metastable crystallographic phases that during sintering act as seeds for the final phases [9]. However, these methods are usually accompanied by rigorous conditions, such as ultra-high pressure, long production cycle and expensive equipments, which limit the wide applications of transparent nanoceramics.

Recent researches indicate that coherent, dense, amorphous bulk alloys and glasses can be successfully densified from amorphous powders by viscous flow within the kinetic window $\Delta T = T_g - T_s$, where T_g is the glass transition temperature and T_s is the starting crystallization temperature [10,11]. Based on these work, we develop a new method of amorphous sintering followed by controlled crystallization (ASCC), in which the amorphous powders are prepared, sintered via viscous flow, and then converted to transparent nanoceramics by heat-treatment. This approach makes densification and grain growth take place through different mechanisms, which can offer the opportunity to control two processes separately. However, only some transparent nanoglass–ceramics have been obtained from glasses by crystallization. This should be attributed to the different crystallization abilities of the multi-component mother glasses, which make it difficult to achieve a high crystallization degree up to 95% by heat-treatment. In the ASCC

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method, eutectic compositions are used to prepare transparent nanoceramics because of their medium glass-forming abilities [12].

In the present work, transparent $LaAlO_3$-based nanoceramic was prepared by the ASCC method as an example. The glass powders with a eutectic composition were prepared, sintered and converted into transparent $LaAlO_3$/t-ZrO_2 nanoceramics via a controlled crystallization process. The feasibility of this method for other systems had also been demonstrated.

2. Experimental

2.1. Preparation

Raw materials used in this study included: Al_2O_3 (purity > 99.99%, D_{V50} = 200 nm, Dalian Luming Nanometer Material Co., Ltd.), La_2O_3 (purity ⩾ 99.99%, D_{V50} = 509 nm, China Minmetals (Beijing) Research Institute) and m-ZrO_2 (purity ⩾ 99.8, D_{V50} = 46 nm, Dongguan SG Ceramics Technology Co., Ltd).

The powder mixtures with a molar composition of 53%Al_2O_3–20%La_2O_3–27%m–ZrO_2 [13] (named hereafter as ALZ) were dispersed as an aqueous suspension with 1.5 wt% polyvinyl alcohol (PVA, molecular weight 1700, purity ⩾ 99.0%, Beijing Chemical Works) as binder, and spray dried into spherical particles. Spray dried agglomerates were feed into a C_2H_2/O_2 flame at a rate of 20 g/min, and then sprayed into water to prepare the ALZ glass microspheres, where the C_2H_2 flow rate was 20 l/min and the O_2 flow rate was 15 l/min. The flame was vertical to the water surface, and produced a combustion temperature up to 3200 °C. The particles were heated, melted and quenched into water to obtain a cooling rate of ~10^3 °C/s. The glass microspheres deposited at the bottom of a steel container were collected, dried and sieved. For hot-pressing, 5.0 g glass powder passed through 500 mesh was loaded into a graphite die (Φ20 mm), the internal surface of which was covered with a graphite sheet to avoid direct contact between the powder compact and the graphite die. The sintering temperature was elevated from room temperature to the final sintering temperature (about 900 °C) at 10 °C/min, and dwelled for several minutes to achieve densification with the aid of a pressure exerted before the dwell. After cooled down, the obtained glasses were heat-treated at different temperatures ranging from 900 °C to 1300 °C to prepare the transparent nanoceramics.

2.2. Characterization

Glass transition temperature (T_g) and starting crystallization temperature (T_s) of the glass microspheres were determined by a differential thermal analysis (DTA, NETZSCH STA 449C, Germany). Phase assemblage was identified by X-ray diffraction (XRD, D8 Focus, Bruker, Germany) using Cu Kα radiation. Microstructure was characterized by scanning electron microscopy (SEM, Hitachi S-4300, Japan), and energy dispersive spectroscopy (EDS, Shimazu 6853-H, Japan) was used to analyze the chemical composition in selected area. The in-line transmittance spectras were obtained using an UV–VIS–NIR Spectrophotometer (Cary 5000, Varian, America) for 175–2000 nm and a Fourier Transform Infrared Spectra (FTIR; Excalibur 3100, Varian, America) for 2000 nm–25 μm. All the samples were polished down to 1 mm thick. According to the mixture rule, the refractive index (n_g) of the ALZ glass is given by [14]:

$$n = \Phi_1 n_1 + \Phi_2 n_2 + \Phi_3 n_3 \quad (1)$$

where n_1, n_2 and n_3 are the refractive indexes of Al_2O_3, La_2O_3 and ZrO_2, respectively, Φ_1, Φ_2 and Φ_3 are the volume fractions of the respective components described above. Therefore, the n_g is 2.00. Based on these results, the theoretical transmittance (T_{th}) of the ALZ glass was calculated as 80% using the relations given in the literature [7]. The sample density was measured by Archimedes method, and the theoretical density of the ALZ glass can be calculated to be 4.56 g/cm^3 by an empirical equation [15]

$$\rho_{th} = 0.53 \cdot \frac{\sum(M_i \cdot x_i)}{\sum(V_i \cdot x_i)} \quad (2)$$

where M_i is molar weight (kg/mol), x_i is molar fraction (mol%), and V_i is packing density parameter (m^3/mol) for an oxide M_XO_Y. Based on the density variation, the degree of crystallization (α) of the heated sample was evaluated as reported in the literature [16]. Vickers hardness (H_v) and fracture toughness (K_{IC}) were measured using a microhardness machine (HXD-1000TM, Shanghai), and by application of 500 gf (4.9 N) load on polished surface for 15 s.

3. Results and discussion

3.1. Preparation of ALZ glass powder

In this study, the eutectic point of the ALZ system is 1665 °C [13]. Although the flame spray process provided a high temperature up to 3200 °C, only smaller spray-dried particles could be heated to a temperature above the melting point during the supersonic spray process. It was found that the ALZ glass powders with particle size below 38.5 μm (−500 mesh) were fully spherical and transparent under an optical microscope because of the higher degree of melting and quenching. Differential Thermal Analysis indicated that the kinetic window (ΔT) of the ALZ amorphous microspheres was 816–895 °C. According to the empirical rule, the sintering temperature is generally chosen to be 20 °C lower than T_s so as to avoid devitrification [17]. Therefore, the optimal sintering temperature for the ALZ system was 875 °C, which is well located in the kinetic window for sintering.

3.2. Sintering of ALZ transparent glass

It is generally considered that the sintering of glass frit into bulk forms is realized by viscous flow within the kinetic window, while the densification rate is positively proportional to the applied pressure P according to the $d\rho/dt = 3P(1-\rho)/4\eta$, where η is the viscosity [18]. Thus, during the sintering process conducted at 875 °C, a pressure ranging from 30 MPa to 90 MPa was applied to achieve full densification as soon as possible. The shrinkage behaviors are shown in Fig. 1. It is observed that the shrinkage process consisted of three stages: accelerating shrinkage, rapid shrinkage and shrink-

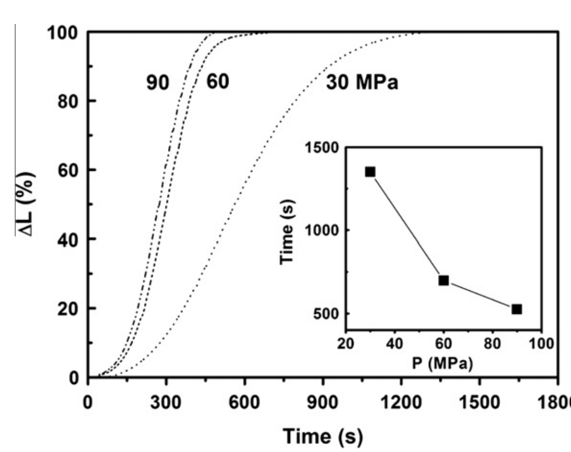

Fig. 1. Shrinkage behavior of ALZ glass powders sintered at different pressures of 30, 60 and 90 MPa. The inset shows the dependence of shrinkage time on applied pressure.