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Short communication

Processing and microstructure of γ-$LiAlO_2$ ceramics

Jiu Lin, Zhaoyin Wen *, Xiaogang Xu, Zhonghua Gu

Key Laboratory of Energy Conversion Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 DingXi Road, Shanghai 200050, PR China

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Abstract

γ-$LiAlO_2$ ceramics with different grain sizes were prepared by controlling the sintering process and regulating the size and shape of the precursor powders. It was found that a size gradation of powders promoted the growth of γ-$LiAlO_2$ grains. Ceramics with an average grain size of 10 μm were prepared from the size-graded powders. It was demonstrated that the shape of the precursor powders greatly affected the grain growth of the ceramics whereas the granulation of the powders restrained the abnormal grain growth. Furthermore nano-sized precursor powders obtained by a sol–gel route made it possible to prepare nano-structured γ-$LiAlO_2$ ceramics.

Keywords: B. Grain size; $LiAlO_2$; Tritium breeder; Microstructure

1. Introduction

γ-$LiAlO_2$ is considered as a promising candidate of tritium breeding material in the fusion energy reactors due to its favorable tritium contribution after neutron irradiation. It is also a good substrate material for the epitaxy of GaN and ZnO crystals because of its optimal structure and thermal stability. Furthermore, γ-$LiAlO_2$ has been used as matrix material in molten carbonate fuel cell and as ceramic filler for the composite electrolytes in lithium secondary battery. The microstructure of γ-$LiAlO_2$ ceramics is an important factor that has great influences in tritium release, thermal stability, and electrochemical performance [1–3]. In addition, the grain size and specific surface of tritium breeders are important parameters for the recovery of tritium according to the diffusivity and release process of tritium in crystal grain [4,5]. Furthermore, it was found that tritium extraction rate of ceramics with small grains was much faster than that of ceramics with large grain size and with the same open porosity [6]. Investigations in the preparation of γ-$LiAlO_2$ powders with different size distributions have been reported these years [7–11]. However, the study on the control of grain size of γ-$LiAlO_2$ ceramics has been seldom reported.

In this paper, the γ-$LiAlO_2$ ceramics with different grain sizes were prepared. The grain size of γ-$LiAlO_2$ ceramics was controlled by the sintering process and the regulation of the size, and shape of powders.

2. Experimental

γ-$LiAlO_2$ powders of micron dimension were prepared by a solid state reaction method. A stoichiometric amount of reagent-grade Li_2CO_3 and γ-Al_2O_3 with the atomic ratio of Li:Al = 1:1 was mixed by ball milling and then calcined at different temperatures in the range of 1073–1273 K for 2 h to prepare γ-$LiAlO_2$ powders with different size distributions. To prepare γ-$LiAlO_2$ ceramics with grain size of ~10 μm, powders of average size 6 μm and 3 μm, obtained at 1273 K and 1173 K respectively, were mixed at the weight ratio of 1:1, pressed to disk-shaped green samples (10 mm in diameter, 2–3 mm in thickness) at 10 MPa and then sintered at 1473 K in air for 4 h. To prepare γ-$LiAlO_2$ ceramics with grain size of ~1 μm, the mixture of Li_2CO_3 and γ-Al_2O_3 were prepared by ball milling and then granulated to ball-shaped particles of 10–20 μm in diameter by spray drying. Then the powders were molded to disks by isostatic pressing at 200 MPa, and sintered at 1473 K in air for 4 h.

The nano γ-$LiAlO_2$ powders were synthesized by a sol–gel approach. A stoichiometric amount of $LiNO_3$ and $Al(OH)_3 \cdot 9H_2O$ with the atomic ratio of Li:Al = 1:1 were

* Corresponding author. Tel.: +86 21 52411704; fax: +86 21 52413903.
E-mail address: zywen@mail.sic.ac.cn (Z. Wen).

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dissolved in water. Then the citric acid was added slowly to the solution at a citric acid:metal cation molar ratio of 2:1. Ammonia was then added to the solution to control the pH value of the solution at around 3. That solution was stirred at 343 K for about 4 h to prepare the sol. The gel precursor was obtained by drying the sol at 393 K for 10 h. The gel was calcined at 1073 K for 4 h, the powders obtained were then dry pressed to disks at 10 MPa and sintered at 1273 K in air for 4 h.

Powder size distribution was characterized with a laser particle size analyzer (Mastersizer2000, Malvern). The microstructures of powders and ceramics were analyzed in detail by electron probe micro analysis (EPMA, JXA-8100, JEOL), transmission electron microscopy (TEM, JEM-2010), and an optical microscope (LW200, Jianduan, Shanghai).

3. Results and discussion

Particle size distributions of two kinds of γ-$LiAlO_2$ powders used to prepare ceramics with grain size of $\sim$10 μm are shown in Fig. 1. It can be found in Fig. 1(a) that the large sized powders had an approximate normal size distribution. The frequency peak around 6 μm indicated the average particle size. As is shown in Fig. 1(b), the small powders had a competitively wide size distribution, d_{50} of which was about 3 μm. Two frequency peaks at around 0.2 μm and 4 μm were also observed, which were taken as the average size of primary particles and aggregates, respectively.

The EPMA fractographs of γ-$LiAlO_2$ ceramics obtained by sintering the size-graded powders are shown in Fig. 2.

Observations showed that the γ-$LiAlO_2$ ceramics composed of the grains of $\sim$10 μm with fused surface. The precursory γ-$LiAlO_2$ powders around 3 μm were rarely found in the final ceramics, but some small grains were observed surrounding the large grains instead, suggesting that the small precursory γ-$LiAlO_2$ powders decreased in size during sintering. At the sintering temperature, the mass transfer from small particles to large particles lead to the growth of the large precursory γ-$LiAlO_2$ particles and the decrease or disappearance of the small particles. The phenomena can be explained by the sintering thermodynamics. In the sintering process of ceramics, the powders tend to grow together through diffusion, leading to the decrease of specific surface and surface free enthalpy. In the primary period of sintering, the solid γ-$LiAlO_2$ particles tend to be semi-melting. This transformation can be proved by the fused grains in γ-$LiAlO_2$ ceramics observed by Sokolov and Stein [12] and Fouad et al. [13]. The surface tension of the different fused particles was approximately thought as the same and therefore the surface free enthalpy could be calculated with the product of the total surface area and the surface tension. When large semi-melting particles surrounded by small ones, the mass diffusion from small particles to large ones

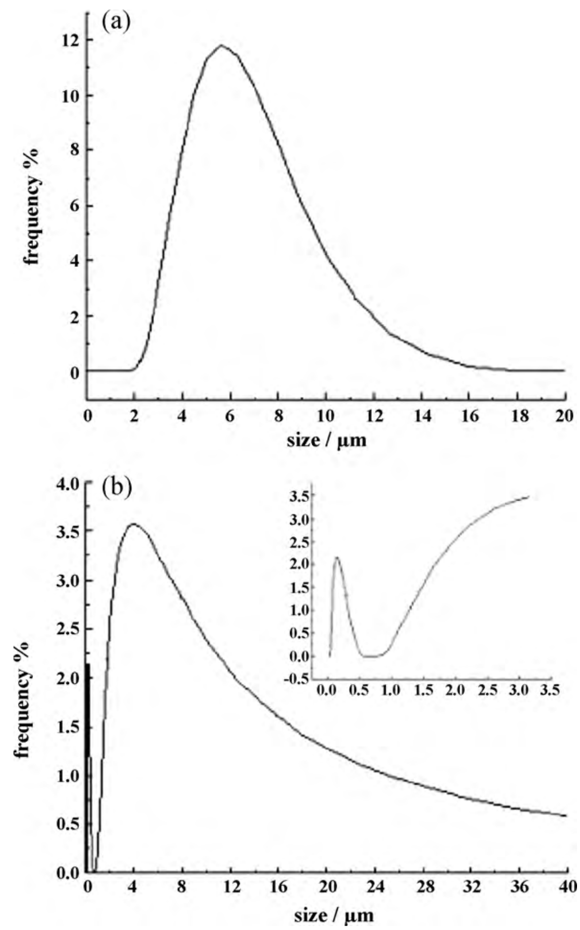

Fig. 1. Particle size distributions of the powders used to prepared γ-$LiAlO_2$ ceramics with large grains.

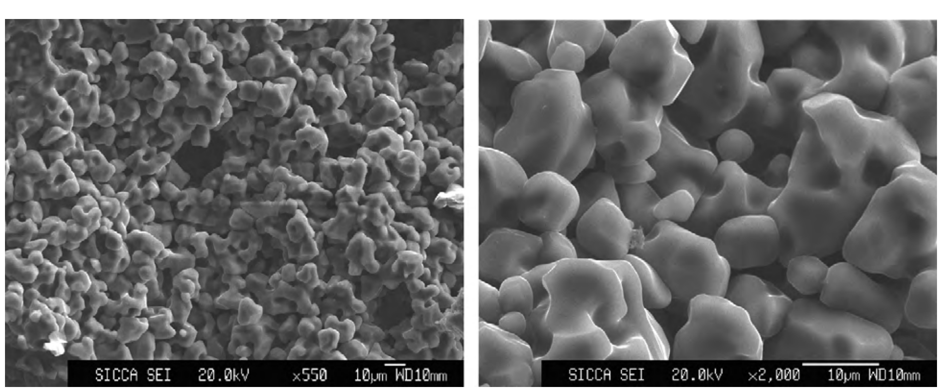

Fig. 2. Fractographs of the γ-$LiAlO_2$ ceramics with large grains.

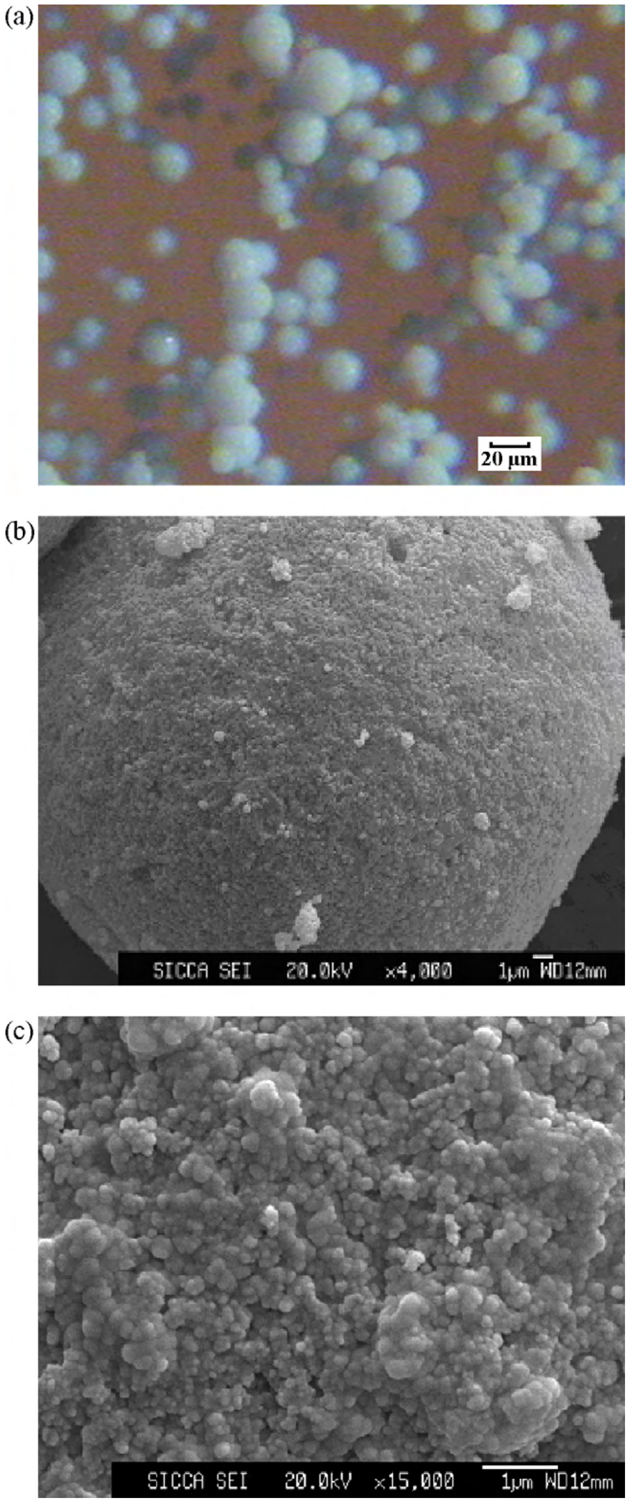

Fig. 3. Morphology of granulated pellets: (a) optical graph; (b) and (c) EPMA graphs.

predominates, resulting in the decrease of the total surface area and the total surface free enthalpy. It can be deduced from the experimental results that it is possible to prepare γ-$LiAlO_2$ ceramics with large grains by size gradation.

The abnormal grain growth discussed above was restrained by pelletizing the precursor powders to the similar size and shape. The optical micrograph and EPMA graphs of particles obtained by spray drying are displayed in Fig. 3. As is shown in the optical micrograph, the precursor powders were granulated to pellets of 10–30 μm in diameter. It can be observed in the EPMA graphs that the pellets were composed of round particles of the similar submicron size.

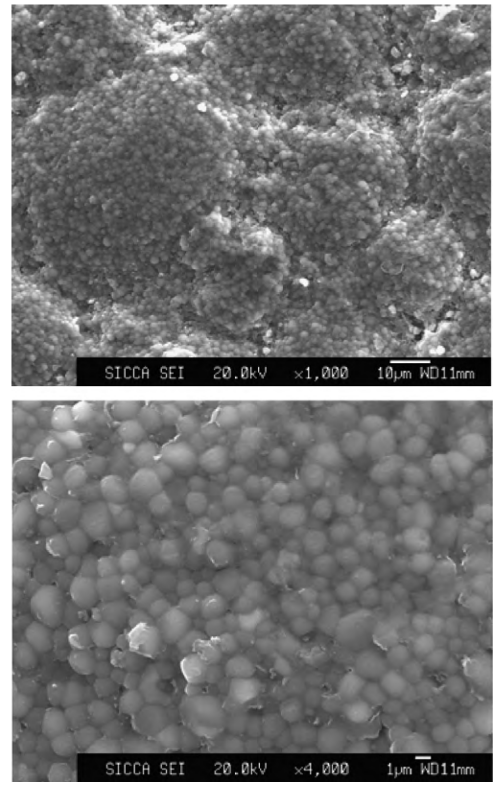

Fig. 4. EPMA graph of γ-$LiAlO_2$ ceramics with grains of micron dimension.

The surface microstructure of the γ-$LiAlO_2$ ceramics after sintering is shown in Fig. 4. It was found that the large pellets granulated from precursory powders were fractured during isostatic pressing. The spherical particles around 1 μm were obtained in the sintered ceramics. The average density of these sintered ceramics was 2.58 g/cm^3 (relative density 98.8%). The spherical γ-$LiAlO_2$ particles were connected to particles around them during sintering, leading to the densification of the ceramics and avoiding the abnormal grain growth. Therefore, it is feasible to restrain the abnormal grain growth in γ-$LiAlO_2$ ceramics by sintering green bodies composed of powders with the similar size and shape. When the powders in the ceramic green body are of the similar size and shape, the merging between particles is difficult to occur. The growth of connection parts between particles predominates in the sintering process instead of merging growth. The connection parts between particles of pellet shape have strong attraction to the particles close to the connection parts due to the surface extension. The order of magnitude of that attraction is as high as 100 kJ/cm^2 when the average diameter of the particles is around 2 μm [14]. The connection parts grow due to that huge attraction, leading to the densification of the ceramic body.

The specific surface area of powders is determined by the particle size. When the average size of γ-$LiAlO_2$ powders is

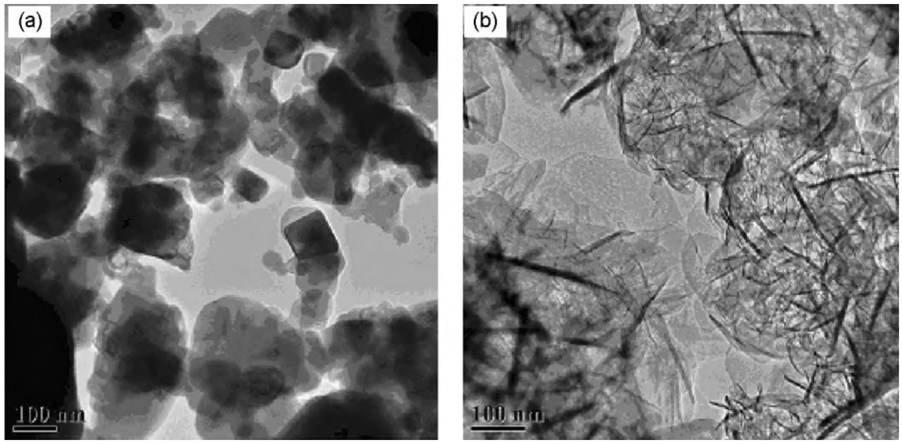

Fig. 5. TEM graphs of the powders prepared by the sol–gel method.

decreased to nanodimension, the high surface free enthalpy brings the good sintering activity of powders and promotes the grain growth at a comparatively low sintering temperature. The growth of large fused grains was expected to be restrained. Therefore, efforts were made to prepare γ-$LiAlO_2$ ceramics with nano-structured grains by sintering green bodies composed of nanoparticles. It is crucial to decrease the particle size of the precursor $LiAlO_2$ powders and enhance the sintering activity. The typical transmission electron microscopy of the powders prepared by the sol–gel method is shown in Fig. 5. It was found that the powders composed of laminar crystals and fine needle-shaped crystals. As is shown in Fig. 5(a), the laminar γ-$LiAlO_2$ particles were 50–100 nm in diameter. While the needle-shaped particles in Fig. 5(b) were as fine as about 10 nm in width and 100 nm in length. It was found that the treating temperature for the gel had remarkable influence in the content of the laminar and needle-shaped particles. The EPMA graphs of fractured surface of the γ-$LiAlO_2$ ceramics sintered from the nanopowders are shown in Fig. 6. The average grains of the ceramics were found to be around 100 nm. Therefore, it is an effective way to prepare γ-$LiAlO_2$ ceramics with fine grains that decreasing the size of the precursor powders by the sol–gel route.

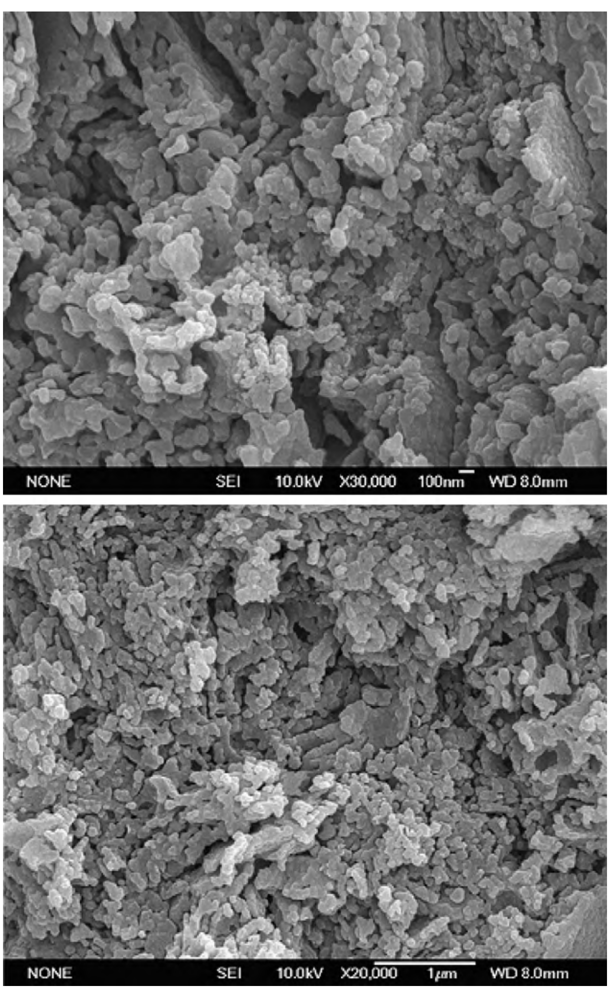

Fig. 6. EPMA graphs of nano-structured γ-$LiAlO_2$ ceramics.

4. Conclusions

γ-$LiAlO_2$ ceramics with different grain sizes were prepared by controlling the sintering process and regulating of the size and shape of the precursor powders. γ-$LiAlO_2$ ceramics with grain size of around 10 μm were prepared by the size gradation process. Ceramics with grains of about 1 μm was obtained by regulating the shape of the precursor particles. Nano-structured γ-$LiAlO_2$ ceramics was prepared with nanopowders synthesized by a sol–gel route.

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