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Fabrication of Li_2TiO_3 ceramic pebbles with fine microstructure by microwave sintering

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ABSTRACT

Lithium metatitanate (Li_2TiO_3) ceramic pebbles were successfully fabricated by microwave sintering using the powders synthesized via solid state reaction. Nano-size Li_2TiO_3 powders with an average particle size of 45 nm were synthesized by solid state reaction, and wet process was employed to fabricate Li_2TiO_3 pebbles with good sphericity. The pebbles were sintered by microwave process with rapid heating rate. Due to the volumetric heating and enhanced diffusion of microwave sintering, the sintered Li_2TiO_3 ceramic pebbles show high density (>85%T.D.), high crush load and uniform microstructure with small grain size (100 nm–1 μm), which might hold good potential in tritium release and long-term stability. The results show that the microwave sintering is a promising process for the fabrication of Li_2TiO_3 pebbles with fine microstructure and good mechanical property.

1. Introduction

Tritium breeder, as a tritium source for fusion power reactors, is considered as a key function material of the Test Blanket Module [1]. The research of the fabrication process and property for tritium breeding materials is of great significance to the development of fusion power reactors [2]. Lithium metatitanate (Li_2TiO_3) has been selected as a promising ceramic breeding material for its good tritium release property, chemical stability, good compatibility with structural materials, and low activation characteristics [3–5]. Extrusion–spheronisation–sintering process [6], wet process [7] and emulsion method [8] have been wildly used for the fabrication of Li_2TiO_3 ceramic pebbles.

The microstructure and properties of ceramic breeder materials have determining effect on tritium release behaver and long-term stability during irradiation [9]. Pebbles with a smaller grain size, and thus a larger number of grain boundaries, should facilitate tritium release [9,10]. The tritium release experiments have shown that tritium release behavior of small grain samples is better than that of coarse grain ones [11,12]. While most of the Li_2TiO_3 ceramic pebbles fabricated and irradiated at present have a grain size in micrometer scale. The fabrication process and properties of pebbles with small grain size (e.g. < 1 μm) is rare. Besides, mechanical property and density are important properties for tritium breeder to withstand the harsh conditions during the reactor cycling [1].

The property of precursor powders and sintering process, are two important steps for fabricating ceramics with fine structure and good property [13]. Nanocrystalline Li_2TiO_3 powders have been synthesized by various methods, such as sol-gel process [14], combustion synthesis [15] and hydrothermal method [10,16]. It is a challenge to synthesize nano-size Li_2TiO_3 powders by solid state reaction [17,18], a simple and efficient powder preparation method. Furthermore, the pebbles were mostly fabricated via conventional sintering process. Microwave sintering, an attractive sintering process, has shown significant advantages against conventional sintering procedures [19–21]. Because of the volumetric heating and enhanced diffusion, the materials by microwave process shown fine microstructure and enhanced mechanical properties. In addition, rapid heating rate can be reached by microwave process, which can suppress the surface diffusion and minimize grain

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growth [22]. However, this method has not been established for the fabrication of Li_2TiO_3 ceramic pebbles.

In the present work, the fabrication process of Li_2TiO_3 ceramic pebbles by microwave sintering was investigated. Nano-size Li_2TiO_3 powders were synthesized via solid state reaction, and then pebbles with good sphericity were obtained by wet process. Finally, microwave sintering was used to fabricate Li_2TiO_3 pebbles, and the influence of sintering temperature on the microstructure, density and crush load of the pebbles was also investigated.

2. Experimental

2.1. Preparation of Li_2TiO_3 powders

The Li_2TiO_3 powders were synthesized by solid state reaction using lithium carbonate (Li_2CO_3) and nano-titania (TiO_2, anatase) as raw materials. The reaction processing steps are shown in Fig. 1. A quantity of lithium carbonate and titanium oxide was mixed by ball milling in alcohol medium, and the homogenous mixture was dried at 70 °C for 24 h. Then the milled powders were calcined at 600 °C for 4 h in air.

2.2. Fabrication of Li_2TiO_3 ceramic pebbles

The ceramic pebbles were fabricated by wet process. The detailed fabrication procedure is shown in Fig. 1. Briefly, the Li_2TiO_3 powders were mixed with dispersant and deionized water, followed by a planetary ball milling, a homogeneous slurry with high solids loading was achieved. Afterwards, the slurry was dropped into liquid nitrogen drop by drop through an injection system and green spheres were formed under the action of surface tension. The freeze green spheres were placed at bibulous paper in air for a certain time and then dried at 70 °C for 24 h. Finally, the green spheres were sintered by microwave process. The microwave frequency was 2.45 GHz, and up to 2.5 kW of microwave power was available. The pebbles were heated at certain temperatures with controlled heating rate (25 °C/min) and maintained for 5 min.

2.3. Characterization

Crystal structure and crystallographic phase analyses were conducted by X-ray diffraction (DX-2700). The microstructure of the powders and sintered pebbles were analyzed by scanning electron microscopy (Model S-4800, Hitachi, Japan). The density of Li_2TiO_3 ceramic pebbles was tested by Archimedes' principle using ethyl alcohol as the immersion medium. The crush load of the sintered Li_2TiO_3 pebbles was measured using a universal material testing machine (SHIMADZU AG-IC) at room temperature, every twenty pebbles with the same diameter of 1.1 mm were selected for a group.

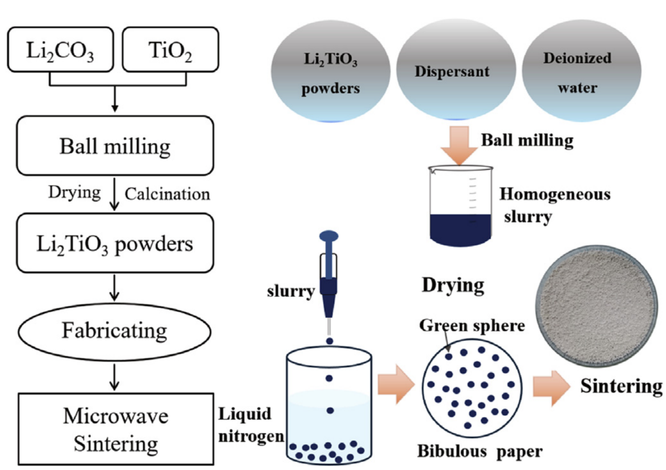

Fig. 1. The fabrication procedures of Li_2TiO_3 ceramic pebbles.

3. Results and discussion

3.1. Phase evolution

The phase evolution of solid state reaction was analyzed by X-ray diffraction. Fig. 2 shows the XRD patterns of the milled precursor powders and synthesized powders by solid state reaction. The precursor powders were made up of Li_2CO_3 and TiO_2, and the crystallite size of TiO_2 was 7 nm estimated from the Scherrer equation. When the precursors were calcined at 300 °C for 4 h, no obvious phase change has taken place. While the temperature was increased up to 400 °C, weak peaks corresponding to monoclinic Li_2TiO_3 phase were emerged due to the following reaction:

$$Li_2CO_3 + TiO_2 \rightarrow Li_2TiO_3 + CO_2\uparrow$$

The formation of Li_2TiO_3 initiates at 400 °C, which is slower than that by traditional solid state reaction [17], by which the phase formation initiates at about 500 °C. The possible reason is that the nano-size titania powders have much surface area and exhibit high reactivity, which might enhance the sintering and crystallization process, thereby decreasing the phase formation temperature.

Further increasing the calcination temperature to 500 °C, the intensity of TiO_2 diffraction peaks became very weak, and the Li_2TiO_3 peaks were sharp and intense. With the increase of calcination temperature to 600 °C, the phase of TiO_2 disappeared. While there are still little weak Li_2CO_3 phase peaks, which might be caused by the excess of raw materials and the CO_2 absorption capability of Li_2TiO_3 material [23].

3.2. Microstructure of Li_2TiO_3 powders

Fig. 3 exhibits the microstructure of the precursor powders and the Li_2TiO_3 powders sintered at 600 °C. As shown in Fig. 3(a), the precursor powders are composed of numerous irregular shaped blocks with a particle size of about several micrometers and many

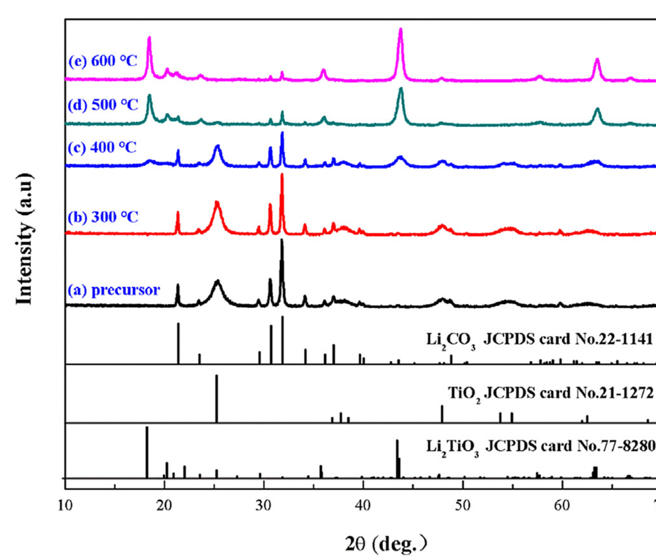

Fig. 2. XRD patterns of Li_2TiO_3 powders synthesized by solid state reaction.