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2018

Gong, Y., Chen, Z., Yang, M., Wang, H., Dang, C., Huang, W., & Lu, T. (2018). A preliminary study on the preparation of nanostructured Ti-doped Li₄SiO₄ pebbles by two-step sintering process. *Ceramics International*, 44(14), 16209-16213. doi:10.1016/j.ceramint.2018.05.252

<https://hdl.handle.net/10356/136732>

<https://doi.org/10.1016/j.ceramint.2018.05.252>

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A preliminary study on the preparation of nanostructured Ti-doped Li_4SiO_4 pebbles by two-step sintering process

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Abstract

Li_4SiO_4 has been widely studied as attractive tritium breeding materials due to its innate merits. Considering the potential advantages of nanostructure in tritium breeding materials, a distinctive process was developed to obtain nanostructured Li_4SiO_4 pebbles. In brief, ultrafine precursor powders were synthesized by solvothermal method without using surfactants, and then indirect wet method was adopted to generate the green spheres with homogeneous microstructure. After that, the suitable sintering conditions were defined by studying the effects of sintering parameters on the grain size evolution, and nanostructured Ti-doped Li_4SiO_4 pebbles were first

obtained by two-step sintering method. This study will be expected to provide references for fabricating other Li-based tritium breeding materials.

Keywords: Tritium breeding materials; Li_4SiO_4 pebbles; Two-step sintering; Ceramic

1. Introduction

Nuclear fusion energy source has been considered as the most ideal and sustainable energy due to its numerous merits, such as clean, safety, high efficiency and abundant fuel resource [1, 2]. As the key part of test blanket module (TBM) in fusion reactor, tritium breeding materials are used to produce the tritium during the fusion reaction process, and thus achieving tritium self-sufficiency [3, 4].

Lithium orthosilicate (Li_4SiO_4) has aroused widely attention because of the high lithium content, low neutron activation rate and favorable tritium release property, and it has been selected as the first candidate in the TBM of helium cooled pebble bed in China and European Union [5-7]. However, Li_4SiO_4 ceramic pebbles widely used at present usually have coarse grains, which may be detrimental to the mechanical property, tritium release behavior and irradiation resistance [8-10]. Moreover, tritium release behavior is greatly influenced by the grain size [11, 12].

Because of the unique properties of nanomaterials, it is believed that nanostructured Li-based ceramics should have distinctive preponderance in the realm of tritium breeding materials. The potential advantages can be concluded as follows: (1) As the grain size dramatically decreases, tritium diffusion distance within the grain is obviously shortened, which is helpful to improve the tritium release rate [13]. (2) Nanoceramics possess abundant grain boundaries, which not only provide more and faster tritium diffusion paths, but also act as pinning sites of radiation defects, thereby enhancing the irradiation resistance of tritium breeding

materials [10]. (3) Due to the fine crystal reinforcing effect, the mechanical strength of the tritium breeding ceramics may also be enhanced [14]. In conclusion, nanocrystallization provides an effective way to improve the mechanical property, tritium release performance and irradiation resistance of tritium breeding materials at the same time, and nanostructured Li_4SiO_4 pebbles are expected to be a promising solid tritium breeder for fusion reactor blanket.

Many methods have been developed to synthesize nanostructured Li_4SiO_4 powders [15, 16], but these methods have not been able to prepare nanostructured Li_4SiO_4 ceramic pebbles so far. For example, Wu et al. successfully prepared Li_4SiO_4 nanopowders by the water-based sol-gel process, but the sintered Li_4SiO_4 ceramics had a grain size of 5~10 μm [15, 17]. A microwave assisted sol-gel synthetic approach was reported by PV Subha et al. to obtain Li_4SiO_4 nanorods as carbon dioxide sorbents [18], but further reports on nanostructured Li_4SiO_4 ceramics had not yet been found. According to the reports and our research results, the main reasons are concluded: (1) Li_4SiO_4 can hardly be directly synthesized by wet chemical methods, and calcination process inevitably results in the coarsening of Li_4SiO_4 ceramic powders, which will further affect the molding and sintering process. (2) Relative high sintering temperature is required to prepare Li_4SiO_4 pebbles with high purity, satisfied relative density and good mechanical strength, but we have to reduce the sintering temperature as much as possible to achieve grain refinement. Hence, there is a narrow temperature window that should be carefully controlled to avoid excessive grain growth. Two-step sintering process, a way to encourage densification and suppress grain growth by manipulating the sintering schedule, has been widely used in the fabrication of nanoceramics [19-21]. However, the relative researches on the fabrication of tritium breeding ceramics have not been reported so far.

In this work, precursor powders were synthesized by solvothermal method in the absence of surfactants, and the mechanism of the mixed solvent was elucidated. Then, indirect wet method was used to generate green spheres. Finally, two-step sintering process was first employed to prepare nanostructured Ti-doped Li_4SiO_4 pebbles. To this end, the effects of sintering parameters (sintering temperature and holding time) on grain size evolution were fully studied to seek an optimal process condition. Based on the above exploration experiments, two distinct conditions were selected to prepare Ti-doped Li_4SiO_4 pebbles. The grain size was statistically measured from the SEM images, and the crush load and relative density were also tested.

2. Experiment

Lithium hydroxide monohydrate was purchased from Alfa Aesar, fumed SiO_2 and TiO_2 were purchased from Aladdin. All chemicals are analytical grade and used without further purification.

2.1 Synthesis of precursor powders via solvothermal method

Lithium hydroxide monohydrate (6.712 g) was uniformly dissolved in 80 ml of methanol under vigorous mechanical stirring (moderate heating is conducive to accelerate the dissolution). Meanwhile, fumed SiO_2 (2.4 g) was dispersed completely in 80 ml of anhydrous ethanol. Then, the above solutions were mixed under stirring to form suspension. Subsequently, the obtained suspension was transferred into a Teflon-lined stainless-steel autoclave (200 ml) and performed at 160 °C for 6 h. Finally, TiO_2 nanopowders (0.16 g) were added into the hydrothermal products and dried at 90 °C without washing to obtain the precursor powders.

2.2 Generation of green spheres via wet method

The as-prepared precursor powders and deionized water were mixed at the mass ratio of 1:1 to get the homogeneous slurry. Immediately, the slurry was dropped into liquid nitrogen through

a nozzle to generate the green spheres under the effects of gravity and surface tension. After for a while, the green spheres were salvaged and dried in air, then stored in drying oven of 60 °C.

2.3 Fabrication of ceramic pebbles by two-step sintering process

Two-step sintering process was investigated to gain nanostructured Ti-doped Li_4SiO_4 ceramics meanwhile maintaining acceptable density and mechanical strength. The green spheres were put into a furnace at a relative high temperature for a short time (first-step), followed by transferring to a furnace with a lower temperature and holding for sufficient time (second-step). Subsequently, it was cooled inside the furnace to room temperature.

2.4 Characterization

Crystal structure and phase purity of the samples were analyzed by X-ray powder diffraction (DX-2700). The morphology and microstructure of the samples were analyzed by scanning electron microscope (Model S-4800, Hitachi, Japan). Grain size of the samples was measured by Nano Measure 1.2 software from SEM images. The density of Ti-doped Li_4SiO_4 pebbles was estimated by Archimedes' principle using ethyl alcohol as the immersion medium. The crush load of Ti-doped Li_4SiO_4 pebbles was measured using a universal testing machine (Instron 5567) with a 0.01 mm/min speed and 10 kN load cell. To eliminate the influence caused by the pebble size, the pebbles with a diameter of about 1.25 mm were used for the test.

3. Results and discussion

Fig. 1 (a) SEM image of the precursor powders, (b) XRD patterns of the precursor powders synthesized by solvothermal method and hydrothermal method

As shown in Fig. 1a, the ultrafine precursor powders were synthesized in the absence of surfactants, which could be ascribed to the advantages of solvothermal method. The methanol/ethanol mixed solvent can preferably dominate the diffusion rate in each direction due to its large viscosity and small surface tension comparing to water, and thus control the growth rate of grains. Additionally, hydroxyl group on the particle surface can be effectively avoided when organic solvent is used as reaction media, thereby improving the particle dispersion. XRD analyses indicate that the precursors consist of lithium metasilicate and lithium carbonate (Fig. 1b, red line). Moreover, the full width at half maximum (FWHM) is wider than that of the sample prepared by hydrothermal method (Fig. 1b, black line), which suggests solvothermal method has advantages over hydrothermal method in the preparation of fine-grain lithium based ceramic powders.

Fig. 2 XRD patterns of the products obtained by calcinating the precursor powders at different temperature

XRD diffractograms of the products obtained by calcinating the precursor powders at different temperature for 4 h were plotted to investigate the phase evolution during the thermal treatment. As shown in Fig. 2, sharp diffraction peaks corresponding to Li_4SiO_4 could be observed clearly in the products, and the amount of residual Li_2CO_3 and Li_2SiO_3 decreased as the calcination temperature rised. Pure Li_4SiO_4 could be obtained when the temperature reached 675 °C. The formation of Li_4SiO_4 could be expressed by the equation ($\text{Li}_2\text{SiO}_3 + \text{Li}_2\text{CO}_3 \rightarrow \text{Li}_4\text{SiO}_4 + \text{CO}_2 \uparrow$) [22]. Moreover, the diffraction peaks shifted slightly toward lower angles when calcination temperature exceeded 625 °C, which was ascribed to the lattice distortion of Li_4SiO_4 caused by doped Ti [23].

Fig. 3 (a) SEM image and (b) element mapping of the cross-section of green spheres

Thanks to the good quality of the precursor powders, the green spheres with homogeneous microstructure were produced by indirect wet method (Fig. 3a). The corresponding element mapping shown in Fig. 3b suggested that TiO_2 nanoparticles were uniformly distributed. And the atomic ratio of Ti to Si was about 1:20, which was consistent with our initial design (Fig. S1 and Table S1). It had been reported that doping TiO_2 nanoparticles could not only inhibit the grain growth during sintering process, but also enhance the mechanical strength of Li_4SiO_4 pebbles [24, 25]. Unfortunately, it was still difficult to attain nanostructured Li_4SiO_4 pebbles by using conventional sintering method. This was mainly because the grain growth of Li_4SiO_4 ceramics, similar with alkali metal ceramics, was sensitive to the sintering temperature [26].

Fig. 4 Particle size as a function of the (a) sintering temperature and (b) dwelling time

To this end, two-step sintering process was tried to prepare nanostructured Ti-doped Li_4SiO_4 pebbles. To seek the suitable processing conditions, grain growth evolution was fully studied, and the details were given in the supporting information (Fig. S2 and S3). To make the results more intuitive, the dependencies of particle size and sintering temperature as well as dwelling time in the first step (denoted by T1 and t1) were plotted in Fig. 4. It was obvious the grain growth largely depended on sintering temperature, and nanograin could hardly be obtained when T1 was higher than 690 °C (Fig. 4a). When t1 was more than 3 min, the grains grew rapidly with dwelling time went on (Fig. 4b). It could be seen from Fig. 4 that the changing curves of particle size with T1 and t1 both matched well with the function (Eq. 1). According to the fitting results, the ultimate sintering temperature and dwelling time for the first step were about 680 °C and 3 min respectively.

$$y = A \exp\left(-\frac{x}{B}\right) + y_0 \quad (1)$$

Where y represented particle size. x represented T1 or t1. A , B and y_0 were both constant.

The effects of sintering temperature and holding time in the second step (denoted by T2 and t2) were further studied by keeping T1 and t1 unchanged (670 °C, 2 min). As shown in Fig. S4, when T2 was less than 600 °C, the ceramic particles contacted loosely, and a mass of pores could be observed, which revealed that the temperature as low as 600 °C was not enough to supply the activation energy for grain boundary diffusion. When T2 raised to 610 °C, the density of the ceramic was improved distinctly, and the grains grew slightly with an average grain size of 70 nm. When the sintering temperature reached 620 °C, the grains sharply grew to about 300 nm. Therefore, to hinder the grain boundary migration (leading to grain growth), T2 should be lower than 620 °C. In addition, it could be seen from Fig. S5 that t2 affected the densification of the ceramic pebbles, but it had less effects on the grain growth. Hence, the optimal sintering temperature for the second step was 610 °C and the appropriate holding time ranged between 8 h and 16 h.

Table 1 Summary of two-step sintering conditions

Conditions	T1	t1	T2	t2
TSS-1	675 °C	2 min	610 °C	16 h
TSS-2	685 °C	2 min	610 °C	16 h

Fig. 5 Cross-section morphologies and grain size distributions of Ti-doped Li_4SiO_4 pebbles prepared through (a) TSS-1 (sample 1) and (b) TSS-2 (sample 2). The inset in Fig. b3 is the digital photo of the sample 2

Fig. 6 XRD patterns of the pestled pebbles obtained by TSS-1 (black line) and TSS-2 (red line)

Based on the above exploration experiments, two-step sintering process was carried out to prepare nanostructured Ti-doped Li_4SiO_4 pebbles in two distinct conditions (see Table 1). The grain size of the samples was derived from the SEM images (Fig. 5). Moreover, the crush load measured by universal material testing machine (see Fig. S6) and the relative density estimated by Archimedes' principle were shown in Table 2. The sample obtained through TSS-1 had a mean grain size of 63.29 nm, average crush load of 11.94 N, and the relative density of 79.17%T.D.. For TSS-2, the crush load (average value 13.63 N) and relative density (81.86%T.D.) were modestly enhanced, but meanwhile the grain size got close to 100 nm. Fig. 6 showed the XRD patterns of the pestled pebbles obtained by TSS-1 and TSS-2. The sharp diffraction peaks of Li_4SiO_4 and weak diffraction peaks of Li_2CO_3 were observed in the diffractogram, indicating the samples prepared by two-step sintering process had relatively high purity. To sum up, two-step sintering process provides a pathway for preparing nanostructured Li_4SiO_4 pebbles as well as other Li-based tritium breeding materials, but fabrication of Li_4SiO_4 pebbles with desirable density and mechanical strength is still a great challenge.

Table 2 Crush load and relative density of Ti-doped Li_4SiO_4 pebbles

Condition	Crush load (N)										Average value	Relative density (%T.D.)
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9	No. 10		
TSS-1	15.66	9.06	14.49	8.02	10.8	12.27	13.62	11.62	—	—	11.94	79.17
TSS-2	9.02	15.75	12.66	16.63	12.01	13.73	15.27	12.58	13.53	15.11	13.63	81.86

4. Conclusions

Ultrafine precursor powders were synthesized by solvothermal process without using surfactants, and then nanostructured Ti-doped Li_4SiO_4 pebbles were obtained by two-step sintering process. The sintering conditions were found by studying the effects of each parameter on the grain size, namely T1 should be below 690 °C, t1 was less than 3 min, T2 could not exceed 610 °C and t2 ranged between 8 h and 16 h. To ensure the acquisition of nanograins, the maximum relative density and crush load of Ti-doped Li_4SiO_4 pebbles (sample 2) were just 81.86%T.D. and 13.63 N. Nevertheless, two-step sintering process provides a feasible route for the fabrication of nanostructured temperature-sensitive materials such as Li-based tritium breeding materials. More importantly, the emergence of nanostructured tritium breeding materials will help us fully understand the effect of grain size on the properties of tritium breeder materials. To meet the increasing requirements of TBM design for tritium breeding materials, enhancing the relative density and crushing strength of the two-step sintering Li_4SiO_4 pebbles will be considered in the following work.

Acknowledgment

This work is supported by the National Magnetic Confinement Fusion Science Program (2014GB125002) and the National Natural Science Foundation of the People's Republic of China (Nos. 11145006 and 91326103). Yichao Gong is thankful for the financial support from China Scholarships Council (CSC Scholarship) and the help from Prof. Zhong Chen in Nanyang Technological University.

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