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Three alternative raw materials for improving the performances of Li_4SiO_4 pebbles

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ABSTRACT

Currently, Li_4SiO_4 has been considered one of the best candidates for tritium breeders. In order to improve the crush load and the density of Li_4SiO_4 pebbles with reasonable pores and small grains for tritium breeding, three alternative raw materials were used for fabricating Li_4SiO_4 pebbles: the fabrication of Li_4SiO_4 pebbles from Li_2CO_3 and SiO_2, the fabrication of Li_4SiO_4 pebbles from Li_2CO_3 and Li_2SiO_3 (for the first time), and the fabrication of Li_4SiO_4 pebbles from Li_4SiO_4. The Li_4SiO_4 pebbles were fabricated by a graphite bed process and sintered in Ar with a series of sintering techniques which based on the different reaction paths deduced from the TG-DTA and XRD results. And they were compared particularly with regard to their effects on the crush load and the density. The results show that the optimal crush load, density, and open porosity of the Li_4SiO_4 pebbles using Li_2SiO_3 and Li_2CO_3 as raw materials reached 64.7 N, 90.3%, and 9.2%, respectively, at sintering technique i, i.e., two holding temperatures (650 and 750 °C) with 5 °C/min heating rate.

1. Introduction

Currently, the deuterium (D)–tritium (T) fusion reactor must include a tritium breeding blanket to produce tritium artificially by neutron irradiation of lithium (Li) because tritium, one of the most important nuclear fuels, is rather scarce in nature. The temperature gradient in the solid breeder blanket varies between 300 °C and 800 °C [1]. Although the pebble bed does not take part in the structural rigidity, it is subject to forces originating from thermal expansion mismatches and suffers from irradiation degradation. These operational conditions imply that the breeders need high mechanical and chemical stability, round shape, and small size, and etc. [2].

Lithium ceramics, such as Li_2O, Li_2TiO_3, Li_2ZrO_3 and Li_4SiO_4, have been proposed as breeder blanket materials [3,4]. Currently, Li_4SiO_4 has been considered one of the best candidates for tritium breeders because of its lithium concentration (0.54 g/cm^3), its high melting temperature (1250 °C), and its excellent tritium release behavior [5]. Helium Cooled Solid Breeder Test Blanket Module (HCSB TBM) in China and EU has selected Li_4SiO_4 ceramic pebble as the breeder material. Different fabrication routes have been investigated to produce the Li_4SiO_4 ceramic pebbles, such as, melt-spraying [6–10], sol–gel [11] and wet methods [12–14]. And the one thing of them in common feature is using lithium hydroxide hydrate, lithium carbonate, or occasionally lithium nitrate as a source of lithium. In terms of the melt-spraying process, pebbles produced from the melt have a higher density [15] and fewer impurities as the melt pot and the impurities of the raw materials are the only two sources of contamination [16]. However, it introduces internal stresses in the pebbles that lead, in some cases, to crack and thus to a deviation in mechanical properties [8]. Moreover, the application of this method was limited due to the harsh function environment and expensive experimental equipment. The common features of sol–gel and wet methods are that they have granulation and sintering process which lead to low density and rough surface. Recently, a graphite bed method (Fig. 1) has been developed [17]. This method is expected to lead to an efficient manufacturing process for mass production as it avoids using organic additives and expensive equipment, i.e. economical and eco-friendly. More importantly, it combined the conventional solid state reaction method to synthesize and fabricate the powders and pebbles of Li_4SiO_4. The conventional solid state reaction has some advantages such as simple to operate and no special needs for experimental conditions.

For tritium recovery purpose pebbles having 80–85% of true density with open porosity (around 10–12%) is required [18]. However, to ensure self-sufficiency of tritium, the breeders must contain as much lithium as possible, which means that the lithium content

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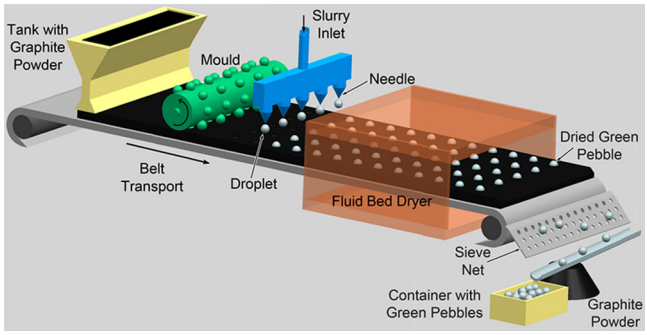

Fig. 1. Schematic diagram of the graphite bed process for pebble fabrication.

and the density of the ceramic breeders should be as high as possible [19]. In the case of tritium diffusion, pebbles with uniform small grain size distribution (blow 10 μm) is preferable [18,19]. In addition, as tons of pebbles would be mounted in the breeding blanket and used for 2 years or more, the pebbles should have high crush load. Therefore, in order to prepare the expected Li_4SiO_4 pebbles for mass production, it is important to investigate the graphite bed method in the fabrication of Li_4SiO_4 pebbles with high density and proper open porosity, high crush load, and small grain size.

In our preliminary work [20], the Li_4SiO_4 pebbles were fabricated by a graphite bed process and sintered at air atmosphere using two different raw materials. In order to further improve the crush load and the density of the pebbles with reasonable pores, the Li_4SiO_4 pebbles were fabricated and sintered at Ar atmosphere using three different starting materials (A: Li_2CO_3 and SiO_2, B: Li_2SiO_3 and Li_2CO_3, C: Li_4SiO_4) and different sintering techniques. In this study, the different sintering techniques had been investigated and compared particularly with regard to their effects on the crush load and density. The aim of this study is to optimize graphite bed process for Li_4SiO_4 pebbles with high density, proper open pores, and high crush load.

2. Material and methods

2.1. Experiment

Analytical reagent (A.R.) grade Li_2CO_3 and SiO_2 were raw materials and purchased from Sinopharm Chemical Reagent Co., Ltd. The Li_4SiO_4 pebbles were fabricated by three different plans. (Plan A): the Li_2CO_3 and the SiO_2 were blended with a molar ratio of 2:1 using deionized water as a milling medium. (Plan B): firstly, the Li_2SiO_3 powder was synthesized at the 750 °C by the solid-state reaction method. Then the Li_2CO_3 and the Li_2SiO_3 were blended with a molar ratio of 1:1 using deionized water as a milling medium. (Plan C): the Li_4SiO_4 powder was synthesized at the 650 °C by the solid-state reaction method. Then Li_4SiO_4 powder was blended with deionized water. The three different slurries were sphered by graphite bed process and sintered with different temperatures.

2.2. Characterization techniques

In order to determine the sintering techniques and understand the reaction mechanisms of Li_2CO_3 and SiO_2 and the reaction mechanisms of Li_2CO_3 and Li_2SiO_3, the Li_2CO_3 with different molar ratio SiO_2 and Li_2SiO_3 were analyzed by thermogravimetry and differential thermal analysis (TG/DTA-DSC) (STA409C NETZSCH, Germany) in Ar atmosphere with a heating rate of 10 °C/min from room temperature to 800 °C. Crystal structures of all samples were investigated by an X-ray diffractometer (D/Max-RB Rigaku, Japan). The microstructures of the pebbles were observed by scanning electron microscope (SEM, JSM-6480LV JEOL, Japan). Crush load of one hundred pebbles were measured by a ceramic strength measuring machine (CDW-5 Changchun Aowei Inc., China) at room temperature.

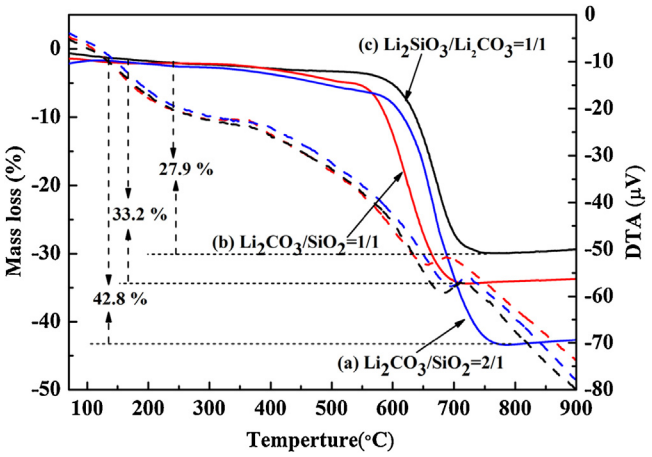

Fig. 2. The TG/DTA curves of the samples: (a) Li_2CO_3 and SiO_2 (2:1), (b) Li_2CO_3 and SiO_2 (1:1), (c) Li_2SiO_3 and Li_2CO_3 (1:1).

3. Results and discussions

3.1. The determination of sintering techniques

The TG-DTA curves were studied to determine the sintering techniques of the pebbles. Fig. 2 shows the results of TG/DTA curves of the samples: (a) Li_2CO_3 and SiO_2 (2:1), (b) Li_2CO_3 and SiO_2 (1:1), (c) Li_2SiO_3 and Li_2CO_3 (1:1). According to the TGA analysis, the overall mass losses of sample (a), sample (b), and sample (c) were about 42.8%, 33.2%, and 27.9%, respectively. The chemical reactions as follows:

$$2Li_2CO_3 + SiO_2 \rightarrow Li_4SiO_4 + 2CO_2 \quad (1)$$

$$Li_2CO_3 + SiO_2 \rightarrow Li_2SiO_3 + CO_2 \quad (2)$$

$$Li_2CO_3 + Li_2SiO_3 \rightarrow Li_4SiO_4 + CO_2 \quad (3)$$

can account for the losses. However, the theoretical weight decreases of Eqs. (1)–(3) were 42.3%, 32.8%, and 26.9%, respectively. The release of pre-adsorbed water may be responsible for the differences. For all samples, weak and broad endothermic peaks between100 °C and 300 °C with ~1.7% weight loss were detected, corresponding to the removal of adsorbed and bonding water. In addition, Tang et al. [21] and Kim et al. [22] found another two mass losses of sample (a) from 700 °C to 900 °C and from 515 °C to 754 °C, respectively. However, in this experiment, for sample (a) from 550 °C to 750 °C, only a sharp weight loss with a broad endothermic peak was found. The reasons for the difference may be caused by the different particle sizes of the raw materials. The average particle sizes of Li_2CO_3 and SiO_2 we used were 1.2 μm and 3.2 μm. In order to further understand the reaction paths of Eqs. (1)–(3), the Li_2CO_3 with different molar ratio SiO_2 and Li_2SiO_3 were calcined at different temperatures and analyzed by XRD. Fig. 3 shows the results of the XRD. And the volume percentage, f, of the compounds (Table 1) determined using the following equation:

$$f = \frac{I_i}{\sum_j I} 100 \quad (4)$$

where I_i represents the integral intensity corresponding to each compound identified, and $\sum_j I$ is the addition of the integral intensity corresponding to all the compounds identified in the sample [23,24]. The f deduced from the Eq. (4) is just a referential value and