Fusion Engineering and Design 89 (2014) 3046–3053

Contents lists available at ScienceDirect

Fusion Engineering and Design

journal homepage: www.elsevier.com/locate/fusengdes

Fabrication of a Li_4SiO_4–Pb tritium breeding material

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ARTICLE INFO

Article history:
Received 17 June 2014
Received in revised form 12 August 2014
Accepted 15 September 2014
Available online 17 October 2014

Keywords:
PbO_2-doped lithium orthosilicate (Li_4SiO_4)
Tritium breeder material
Pebble fabrication

ABSTRACT

PbO_2-doped Li_4SiO_4 pebbles were successfully fabricated by a liquid-atmosphere sintering process. Those pebbles sintered at 1000 °C under atmospheric conditions were found to have an average diameter of 1.05 mm, a sphericity of 98%, a theoretical density of 90.9%, an average crush load of 24.3 N, and a main phase structure of Li_4SiO_4 with a small percentage of Li_8PbO_6. Subsequent optimization of this fabrication process yielded ceramic pebbles suitable for tritium breeding in a test blanket module (TBM).

1. Introduction

Since the 1970s, there have been a number of studies worldwide into using the unique properties offered by various materials for tritium breeding. This has included the high lithium density of Li_2O, the neutron multiplication of Li_2ZrO_3, the good stability of γ-LiA1O_2; not to mention the currently favored candidates for the International Thermonuclear Experimental Reactor (ITER), Li_4SiO_4 and Li_2TiO_3. These in-depth studies have helped to build a comprehensive understanding of such materials by defining such aspects as suitable preparation processes, irradiation properties, tritium release characteristics, tritium retention characteristics and their tritium breeding ratio. However, ternary-lithium-ceramic tritium breeder materials have not yet been proven to meet the strict requirements of future fusion energy reactors [1–4].

Past studies have shown that the addition of soluble oxides (e.g., Al_2O_3 [5], TiO_2 [6,7], PbO_2 [8–10] or Cr_2O_3 [11]) to a lithium-bearing ceramic tritium breeder material can improve its radiation resistance, enhance its compatibility with neutron multiplication agents, and change inherent properties such as its tritium release. In Japan, Lithium-excess Li_{2+x} TiO_3 ceramic pebbles [12–14] have been developed that represent a new generation of advanced tritium breeder, based on the Li_2TiO_3 [3,4,15] tritium breeder material characteristics preferred by its test blanket module (TBM). Furthermore, the wet process was developed to resolve the issue of Li_2TiO_3 instability under a reducing atmosphere, adapt to the design of water cooled blanket and the relatively low tritium breeding ratio [16,17]. This not only improves the overall tritium breeding ratio of the material, but also the lithium density. The poor mechanical strength and stability of the Li_4SiO_4 ceramic pebbles have also been addressed by doping them with TiO_2 or adding an excess of SiO_2 at Forschungszentrum Karlsruhe (FZK) [18–21]. The present focus is therefore on further developing and improving these ceramic tritium breeder pebbles through a melting/spraying process [19–24].

For the next generation of advanced tritium breeder materials, it is essential to overcome the reliability and stability issues currently faced during long-term use in the tritium breeding envelope of a fusion reactor. This paper therefore explores the possibility of using liquid sintering to create stable, Pb-doped Li_8PbO_6 through a solid-phase reaction between LiOH and PbO_2. The influence of various factors such as the relative amount of each component, sintering atmosphere and sintering temperature is also assessed with a view toward establishing the optimal process conditions for a new-type of tritium breeder.

2. Experimental

2.1. Preparation of Li_4SiO_4–Pb precursor powders

A precursor powder was prepared by first placing Li_4SiO_4, LiOH and PbO_2 powders into a planetary ball mill, and then wet-grinding for 4 h. After freeze drying, the mixed precursor powder was placed into a muffle furnace and calcined at 650 °C to remove any

Abbreviations: TBM, test blanket module; SEM, scanning electron microscope; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction; DSC, differential scanning calorimetry.

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http://dx.doi.org/10.1016/j.fusengdes.2014.09.008
0920-3796/

residual water. It was then calcined under atmospheric conditions for a further 24 h at 700 °C to obtain the final Li_4SiO_4–Pb precursor.

2.2. Preparation of Li_4SiO_4–Pb ceramic microspheres

The as-prepared Li_4SiO_4–Pb precursor was ground and mixed with a polymer binder in a planetary ball mill to achieve a relatively stable slurry suspension slurry. From this, Li_4SiO_4–Pb ceramic pebbles were initially produced by a wet-freezing molding process, with the final Li_4SiO_4–Pb ceramic pebbles then obtained through sintering at various pre-programmed temperatures under different atmospheres.

2.3. Performance testing

The reaction temperature of the Li_4SiO_4, LiOH and PbO_2 mixture was evaluated on the basis of its phase-transition temperature using a simultaneous thermal analyzer (Labsys evo, Setaram).

The macroscopic shape, degree of sphericity, microstructure and crystal size of the pebbles was determined using a Hitachi TM-1000 scanning electron microscope (SEM). The shape and sphericity was also assessed by optical microscopy (KEYENCE VH-S30), wherein its diameter in three directions (d_1, d_2 and d_3, where $d_1 > d_2 > d_3$) was used to define a degree of sphericity with a ratio of $(d_1/d_2 + d_2/d_3 + d_1/d_3)/3$. Random measurements of the pebble diameter using a digimatic caliper (accuracy = 0.01 mm) were also used to obtain the particle size distribution. The crystalline phase structure of the ceramic microspheres and raw materials was analyzed by a DX-2500 X-ray diffraction spectrometer.

To determine the maximum crushing load that the ceramic pebbles could sustain within a range of 0–125 N at room temperature, a MTS RT/5 electronic universal material testing machine was used with a loading rate of 0.5 mm/min. A total of 100 pebbles were tested per group, from which the mean value and standard deviation of the crushing load was calculated.

3. Results

3.1. Surface morphology of Li_4SiO_4–Pb pebbles

Fig. 1 shows the surface morphology of a batch of Li_4SiO_4–Pb pebbles, the light brown color of which is the result of the brown PbO powder used in their fabrication.

3.2. Differential scanning calorimetry analysis of Li_4SiO_4–Pb pebbles

The simultaneous thermal analysis results of Li_4SiO_4–Pb are shown in Fig. 2, in which three peaks are clearly discernible at 860, 1033 and 1268 °C. From differential scanning calorimetry (DSC) and X-ray diffraction (XRD) analysis, it is known that the endothermic peak at 860 °C is attributable to $Pb_3Si_2O_7$. Furthermore, the phase transition evident at 1033 °C is caused by the formation of Li_8PbO_6 and Li_4PbO_4 during sintering, whereas the maximum endothermic peak at 1268 °C is due to the formation of Li_4SiO_4. This discrepancy with the typical Li_4SiO_4 formation temperature (1250 °C) is considered to be caused by the presence of PbO_2.

3.3. Morphology of Li_4SiO_4–Pb pebbles

SEM images of Li_4SiO_4–Pb formed under different temperatures and sintering atmospheres are shown in Fig. 3, with Table 1 providing their specific parameters.

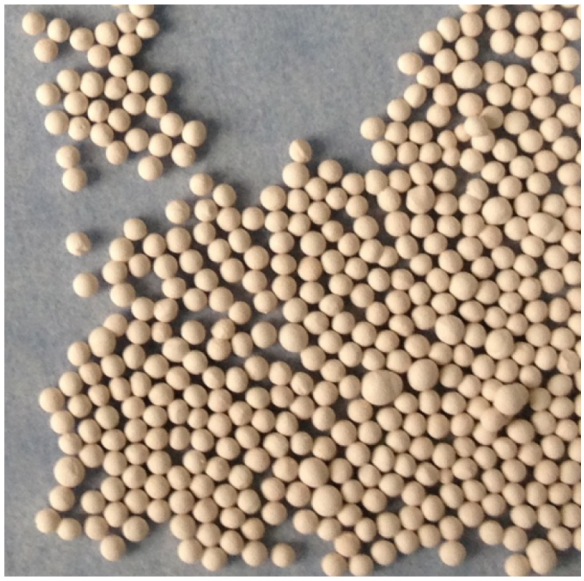

Fig. 1. Macroscopic photos of Li_4SiO_4–Pb pebbles.

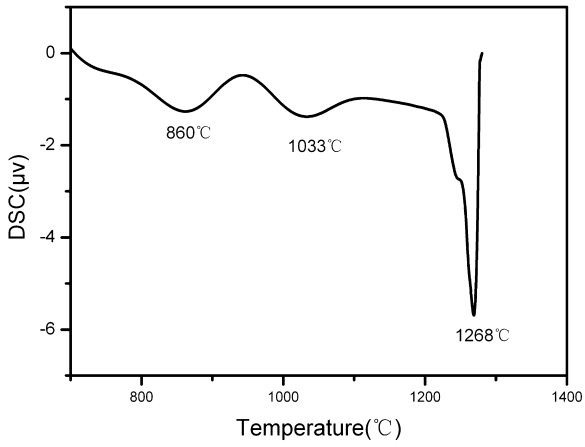

Fig. 2. DSC curve of Li_4SiO_4–Pb pebbles.

Table 1
Sintering temperature and atmosphere.

S/N	Sintering temperature (°C)	Sintering conditions	Sintering time (h)
a	650	Air, tube furnace	12
b	800	Oxygen, tube furnace	2
c	950	Oxygen, tube furnace	2
d	1000	Oxygen, tube furnace	2

3.4. XRD analysis of Li_4SiO_4–Pb pebbles

XRD patterns showing the crystalline phases of Li_4SiO_4–Pb formed under different sintering temperatures and atmospheres are shown in Fig. 4, with their respective reaction conditions and product composition shown in Table 2.

3.5. Crush load of Li_4SiO_4–Pb pebbles

The average crush load of Li_4SiO_4–Pb, as calculated from 50 individual pebbles, is shown Fig. 5. By comparing this with the crush load of Li_4SiO_4 pebbles at different sintering temperatures in Fig. 6,