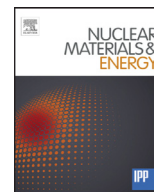




Contents lists available at ScienceDirect

Nuclear Materials and Energy

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

Pebble fabrication of super advanced tritium breeders using a solid solution of $\text{Li}_{2+x}\text{TiO}_{3+y}$ with Li_2ZrO_3

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ARTICLE INFO

Article history:

Available online xxx

Keywords:

Advanced tritium breeder

Solid solution

 Li_2TiO_3 Li_2TiO_3 with excess Li $\text{Li}_{2+x}\text{TiO}_{3+y}$ with Li_2ZrO_3

ABSTRACT

Lithium titanate with excess lithium ($\text{Li}_{2+x}\text{TiO}_{3+y}$) is one of the most promising candidates among advanced tritium breeders for demonstration power plant reactors because of its good tritium release characteristics. However, the tritium breeding ratio (TBR) of $\text{Li}_{2+x}\text{TiO}_{3+y}$ is smaller than that of e.g., Li_2O or Li_8TiO_6 because of its lower Li density. Therefore, new Li-containing ceramic composites with both high stability and high Li density have been developed. Thus, this study focused on the development of a solid solution with a new characteristic. The solid-solution pebbles of $\text{Li}_{2+x}\text{TiO}_{3+y}$ with Li_2ZrO_3 ($\text{Li}_{2+x}(\text{Ti,Zr})\text{O}_{3+y}$), designated as LTZO, were fabricated by an emulsion method. The X-ray diffraction patterns of sintered LTZO pebbles are approximately the same as those of $\text{Li}_{2+x}\text{TiO}_{3+y}$ pebbles, and no peaks attributable to Li_2ZrO_3 are observed. These results demonstrate that LTZO pebbles are not a two-phase material but rather a solid solution. Furthermore, LTZO pebbles were easily sintered under air. Thus, the LTZO solid solution is a candidate breeder material for super advanced (SA) tritium breeders.

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1. Introduction

Demonstration power plant (DEMO) reactors require deuterium and tritium as fuel. However, tritium does not exist in nature; thus, it must be produced in a reactor by neutron irradiation of lithium (Li). Lithium compounds comprising ternary oxides (LiAlO_2 , Li_4SiO_4 , Li_2ZrO_3 and Li_2TiO_3) have been proposed as tritium breeding materials [1]. Among these, lithium titanate (Li_2TiO_3) is one of the most promising candidates for tritium breeding materials for DEMO reactors because of its good tritium release characteristics. The addition of hydrogen to an inert sweep gas has been proposed as a method for enhancing tritium release from tritium breeders. However, the mass of Li in tritium breeders decreases under a hydrogen atmosphere because of Li evaporation and burn-up [2].

To prevent the loss of Li at high temperatures, Li_2TiO_3 with excess Li ($\text{Li}_{2+x}\text{TiO}_{3+y}$) has been developed as an advanced tritium breeder material [3–5]. $\text{Li}_{2+x}\text{TiO}_{3+y}$ exhibits relatively greater stability at high temperatures under a hydrogen atmosphere. In ad-

dition, granulation technology of $\text{Li}_{2+x}\text{TiO}_{3+y}$ has been established by an emulsion method, and major granulation parameters such as diameter, sphericity, density, grain size, molar ratio (Li/Ti), crystal structure, and crush load have been determined to deduce optimal values [6–7].

Although $\text{Li}_{2+x}\text{TiO}_{3+y}$ pebbles have been recognized as a prominent candidate material because of their chemical stability and good tritium release, the tritium breeding ratio (TBR) of $\text{Li}_{2+x}\text{TiO}_{3+y}$ is smaller than that of e.g., Li_2O or Li_8TiO_6 because of its lower Li density. Therefore, new Li-containing ceramic composites with both high stability and high Li density have been developed. Two-phase mixtures such as mixtures of Li_4SiO_4 and Li_2TiO_3 have recently been developed as tritium breeder materials [8]. However, such two-phase mixtures have both advantages and disadvantages over other materials.

The present study focuses on the development of a solid solution with a new characteristic. In a previous study, various solid solution of ternary lithium oxides have been studied as electrode materials for Li-ion batteries [9–10]. Because the ionic radii of Ti and Zr are similar, the possibility of using $\text{Li}_{2+x}\text{TiO}_{3+y}$ with Li_2ZrO_3 ($\text{Li}_{2+x}(\text{Ti,Zr})\text{O}_{3+y}$), designated as LTZO, solid solution as a super advanced (SA) tritium breeder material is surveyed.

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Please cite this article as: T. Hoshino, Pebble fabrication of novel advanced tritium breeders using a solid solution of $\text{Li}_{2+x}\text{TiO}_{3+y}$ with Li_2ZrO_3 , Nuclear Materials and Energy (2016), <http://dx.doi.org/10.1016/j.nme.2016.05.004>

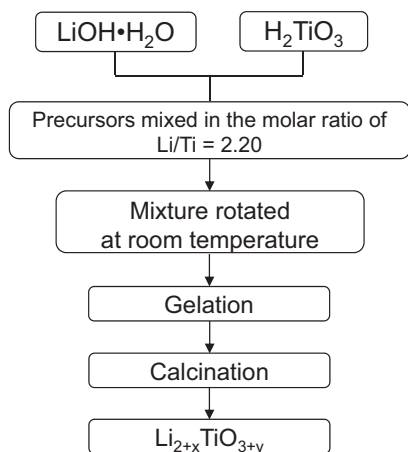
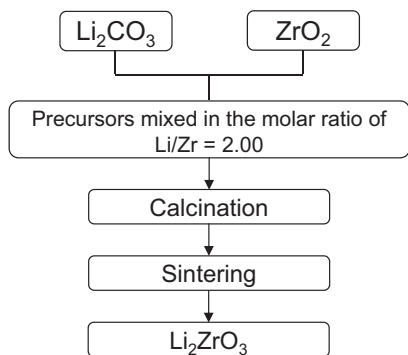
(a) Li_2TiO_3 with added Li ($\text{Li}_{2+x}\text{TiO}_{3+y}$)(b) Li_2ZrO_3

Fig. 1. Flow sheet of the solid-phase reaction processing steps.

2. Experimental

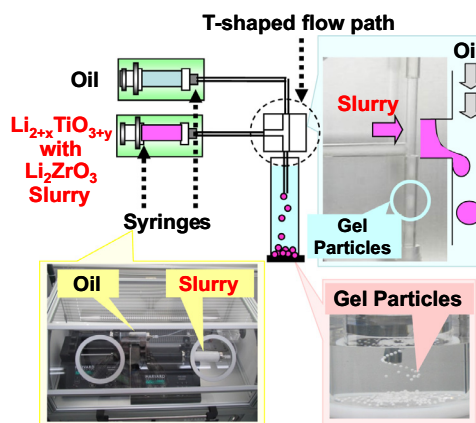
2.1. Raw material preparation

Li_2TiO_3 with excess Li ($\text{Li}_{2+x}\text{TiO}_{3+y}$) was synthesized by a novel solid-phase reaction. Powders of $\text{LiOH}\cdot\text{H}_2\text{O}$ and H_2TiO_3 were mixed in a proportion corresponding to a molar ratio Li/Ti of 2.20. Mixtures of starting powders were continuously rotated using a rotary mixing device at room temperature for 48 h in a polyethylene container. The mixtures were then gradually converted into a gel by solid-phase reactions at room temperature. Thereafter, the gel was dried at 353 K for 24 h in an electrical air oven and subsequently, it was calcined at 973 K for 5 h in air.

Li_2ZrO_3 was synthesized by a standard solid-phase reaction. Powders of Li_2CO_3 and ZrO_2 were mixed in a proportion corresponding to a molar ratio Li/Zr of 2.00. Mixtures of starting powders were continuously mixed at room temperature for 24 h using a ball mill. Thereafter, the mixtures were calcined at 973 K for 5 h in air and sintered at 1273 K for 5 h in air. These solid-phase reaction processing steps are shown in Fig. 1.

2.2. Pebble Fabrication by Emulsion Method

The emulsion method is illustrated in Fig. 2. The granulator used in these experiments comprised two syringes arranged in a T-shaped flow path. One syringe was filled with oil, and the other was filled with the slurry containing $\text{Li}_{2+x}\text{TiO}_{3+y}$ and Li_2ZrO_3 . The slurry was prepared from $\text{Li}_{2+x}\text{TiO}_{3+y}$ powder, binder (agar), and

Fig. 2. Illustrations of $\text{Li}_{2+x}\text{TiO}_{3+y}$ with Li_2ZrO_3 pebble fabrication by the emulsion method.

water. These mixtures were mixed in a ball mill at 323 K for 24 h. The two flow lines from the syringes were connected in a T-shaped flow path, which allowed the slurry flow to be mixed with oil from the oil-filled syringe. Details of pebble fabrication by emulsion method were described in a previous study [11].

The size of the resulting spherical tritium breeder gel particles was controlled by adjusting the oil and slurry flow rates. The gel particles were deposited in an oil-filled container. After granulation, the gel particles were cooled down in the container around a 283 K cooling water pool for 3 h. The obtained gel particles were subsequently calcined at 873 K for 5 h in air and sintered at 1373 K for 5 h in air to control their grain size.

The solid-solution pebbles of LTZO fabricated by an emulsion method are designated as LTZO10 ($\text{Li}_{2+x}\text{TiO}_{3+y}$ with 10 wt% Li_2ZrO_3 added) and LTZO20 ($\text{Li}_{2+x}\text{TiO}_{3+y}$ with 20 wt% Li_2ZrO_3 added). Their particle diameter and sphericity were measured by optical microscopy. The density of the sintered pebbles was measured using the mercury intrusion technique. The grain size was analyzed by scanning electron microscopy (SEM). The actual Li/Ti mole ratio was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The crush load was measured using a universal testing machine. The crystal structure was analyzed by powder X-ray diffraction (XRD).

3. Results and discussion

3.1. Sintering conditions

The predominant factor affecting grain growth was assumed to be the presence of a binder in the gel particles. The binder includes carbon (C) and oxygen (O), and CO_2 is generated by the pyrolysis of the binder. CO_2 reacts with excess Li in $\text{Li}_{2+x}\text{TiO}_{3+y}$ during sintering over 1073 K in air and generates Li_2CO_3 , which promotes grain growth. In the case of $\text{Li}_{2+x}\text{TiO}_{3+y}$, to inhibit the generation of Li_2CO_3 , the calcined $\text{Li}_{2+x}\text{TiO}_{3+y}$ pebbles were sintered at 1073 K for 3 h under vacuum and subsequently sintered at 1323 K for 5 h under a 1% H_2 -He atmosphere [12].

Generated CO_2 did not react with excess Li in LTZO during sintering in air and did not generate Li_2CO_3 . Therefore, the calcined LTZO pebbles were sintered at 1373 K for 5 h in air. Residual Li_2CO_3 was not observed on the surfaces or in the cross-sections of the sintered LTZO pebbles. Fig. 3 shows the sintering conditions of the $\text{Li}_{2+x}\text{TiO}_{3+y}$ pebbles and LTZO pebbles. The LTZO pebbles were more easily sintered under air compared to $\text{Li}_{2+x}\text{TiO}_{3+y}$ pebbles.

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