Journal of Nuclear Materials 459 (2015) 235–240

Contents lists available at ScienceDirect

Journal of Nuclear Materials

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

Reprocessing of lithium titanate pebbles by graphite bed method

Ming Hong, Yingchun Zhang *, Maoqiao Xiang, Yun Zhang

School of Materials Science and Engineering, University of Science and Technology Beijing, 30 Xueyuan Road, Haidian District, Beijing 100083, PR China

ARTICLE INFO

Article history:
Received 29 August 2014
Accepted 20 January 2015
Available online 28 January 2015

ABSTRACT

Lithium titanate enriched by ^{6}Li isotope is considered as a candidate of tritium breeding materials for fusion reactors due to its excellent performance. The reuse of burned Li_2TiO_3 pebbles is an important issue because of the high costs of ^{6}Li-enriched materials and waste considerations. For this purpose, reprocessing of Li_2TiO_3 pebbles by graphite bed method was developed. Simulative Li_2TiO_3 pebbles with low-lithium content according to the expected lithium burn-up were fabricated. After that, Li_2TiO_3 pebbles were re-fabricated with lithium carbonate as lithium additives, in order to gain the composition of lithium titanate with a Li/Ti ratio of 2. The process was optimized to obtain reprocessed Li_2TiO_3 pebbles that were suitable for reuse as ceramic breeder. Density, porosity, grain size and crushing load of the reprocessed pebbles were characterized. This process did not deteriorate the properties of the reprocessed pebbles and was almost no waste generation.

1. Introduction

In the first generation fusion reactors, the fusion of deuterium and tritium is considered to produce energy to meet the future energy demand. It is necessary to produce tritium artificially because there is no naturally available tritium source. Lithium isotope (^{6}Li) has the ability to produce tritium through neutron nuclear reaction. Thus Li-based ceramics enriched by ^{6}Li isotope are considered for the tritium generation in future fusion reactors [1,2]. Lithium titanate is one of such Li-based ceramic material being considered for its attractive properties, such as high thermal and chemical stability, high thermal conductivity, and low tritium solubility [3–5].

It was reported that the lithium burn-up of ceramic pebbles in the fusion reactor will be limited to about 15% [6,7]. Considering the large amount of ^{6}Li-enriched breeder materials will be used in fusion reactors, reprocessing of the used material is essential due to the high costs of ^{6}Li and waste disposal considerations [8,9]. A lot of works were carried out to reprocess Li_2TiO_3 ceramic. Alvani et al. [7,10] recovered Li-value from Li_2TiO_3 powder and pebbles in aqueous solution of hydrogen peroxide with acid additive. Li_2TiO_3 pebbles were successfully re-fabricated from the dissolved solution either by citric acid or sol–gel route. Tsuchiya et al. [11,12] fabricated Li_2TiO_3 pebbles by wet process using lithium titanate solution. The dissolving process and sintering condition were optimized. Lagos and Becerra [13] proposed a method to recover lithium carbonate from Li_2TiO_3 pebbles by a dissolution and precipitation process. Hoshino et al. [14,15] studied the dissolving ability of lithium titanate by using different chemical reagents and recovered Li-value in the form of lithium hydroxide. Mandal [16] recovered Li-value as lithium carbonate from Li_2TiO_3 pebbles by using diluted hydrochloric acid. The experimental parameters, such as concentration and temperature, were discussed in detail.

In the previous studies, a wet chemical process was involved to the reprocessing of Li_2TiO_3 ceramic. Some of these processes required complex recycling processes and consumed huge amounts of reagents. According to the details given in [10,16], dissolving only 1 kg of lithium titanate need 12–20 l of solvent in dissolution step. The subsequent reprocessing of effluent was necessary for effective use of resources and reduction of pollution. To date, reprocessing of Li_2TiO_3 pebbles without any additional wet chemical recycling step has not been reported, which may provide a simple and facile reprocessing method.

In our previous study, Li_2TiO_3 pebbles were fabricated by a graphite bed method [17]. This method avoided the use of chemical additives that was usually used in wet process, and was expected to simplify the process of Li_2TiO_3 pebbles reprocessing. In this paper, Li_2TiO_3 pebbles with low-lithium content were fabricated to simulate the burned pebbles with expected lithium end-of-life burn-up. Li_2TiO_3 pebbles were re-fabricated with an addition of lithium carbonate to gain the composition of lithium titanate with a Li/Ti ratio of 2. Any possible changes in the properties due to reprocessing were investigated by TG–DTA, XRD, SEM, etc.

* Corresponding author. Tel./fax: +86 10 62334951.
E-mail address: zycustb@163.com (Y. Zhang).

http://dx.doi.org/10.1016/j.jnucmat.2015.01.041
0022-3115/

2. Experimental

2.1. Materials and methods

Raw materials were analytical grade lithium carbonate (Li_2CO_3) and titanium dioxide (TiO_2), purchased from Sinopharm Chemical Reagent Co., Ltd. As costs had to be saved and the isotope ratio was not supposed to have any influence on the fabrication process or properties of the pebbles, the experiment was carried out by using natural enriched lithium carbonate (7.5 at.% ^6Li). Powder mixtures of Li_2CO_3 and TiO_2 were calcined under air at 700 °C for 4 h. Two kind of lithium titanate powders with Li/Ti ratio of 1.7 and 2.0 were prepared by solid-state reaction according to chemical reaction (1) and (2), respectively.

$$0.85Li_2CO_3 + TiO_2 \rightarrow 0.75Li_2TiO_3 + 0.05Li_4Ti_5O_{12} + 0.85CO_2 \quad (1)$$

$$Li_2CO_3 + TiO_2 \rightarrow Li_2TiO_3 + CO_2 \quad (2)$$

Simulated Li_2TiO_3 pebbles were fabricated by graphite bed method using the non-stoichiometric powder. Details of this method have been described in elsewhere [17]. The simulated pebbles were sintered at 1200 °C for 2 h and annealed at 1000 °C for 100 h to provide composition homogeneity and structure stability. The average diameter and grain size of the simulated pebbles were 1.0 mm and 25 μm, respectively.

The simulated lithium titanate pebbles were mixed with lithium carbonate to adjust the Li/Ti molar ratio to 2. The mixture were added into deionized water, and then milled in a planetary ball mill using zirconia ceramics as ball mill media for 2 h to obtain homogenous ceramic suspensions. Then green pebbles were formed by use graphite bed method. The green pebbles were calcined at 650 °C for 2 h and then sintered at 1100 °C for 5 h. The Li_2TiO_3 pebbles used as reference pebbles were fabricated by graphite bed method using the stoichiometric powder and sintered at 1100 °C for 5 h.

2.2. Characterization

The morphology of Li_2TiO_3 pebbles was studied by photographic analysis. Thermal behavior of the green pebbles was analyzed by thermogravimetric analyzer appending differential thermal analysis (TG–DTA) at a constant heating rate of 10 °C/min from room temperature to 1000 °C in flowing air (100 ml/min). Crystallographic phase analysis was conducted by X-ray diffraction (XRD) at room temperature using Cu Kα radiation. XRD diffractograms were analyzed by corresponding Joint Committee on Powder Diffraction Standards (JCPDS) by virtue of MDI Jade 5.0 software. The impurities were measured with an atomic emission spectrometer fitted with inductively coupled plasma (ICP-AES). Microstructure was observed by scanning electron microscope (SEM) after being covered with gold to prevent the lack of conductivity. The grain size of the pebbles was measured from SEM photographs. Density was measured by Archimedes' principle using ethyl alcohol as immersion medium. The volume of pebbles was recorded immediately after had been immersed in ethanol to minimize the error caused by the permeability of ethanol. Packing density was measured in a graduated cylinder by tap density instrument. Open porosity was measured by mercury porosimetry. Closed porosity was calculated from density and open porosity. The crush load of a single pebble was measured with an unconfined compression tester with a compression indenter made of SiC.

3. Results and discussion

3.1. Pebbles formation

The morphology of Li_2TiO_3 green pebbles reprocessed by graphite bed method is presented in Fig. 1. The shape of green pebbles was nearly spherical and the diameter was about 1.3–1.5 mm and 1.4 mm on an average. The green pebbles had intact appearance, no broken pebbles were observed. In previous work, Li_2TiO_3 pebbles were prepared by graphite bed process using insoluble lithium titanate as raw material [17]. This experiment illustrated that lithium carbonate additive did not bring adverse effect on pebble formation, although part of lithium carbonate dissolved in water. Graphite powder only remained on the surface of the pebbles due to its intrinsic hydrophobic properties. This phenomenon was beneficial to the removal of graphite powder. During calcining and sintering process, the graphite powder oxidized rapidly in air atmosphere without internal stress produced.

The microstructure of the green pebbles was examined by SEM. Fig. 2 presents the fracture appearance of the green pebbles. As seen in secondary electron image, the green pebbles had a uniform structure. The particle size distribution ranged from 0.3 to 3 μm. Small particles filled in the pores among large particles and formed a close packing. The grain size was effectively reduced by milling process, and small grain size was expected to be beneficial to the sintering process. There was a small amount of interconnected pores, which was less than 1 μm, scattered among the particles. The pores in this structure were generated from combination of non-optimized particles packing and preserved voids which were originally occupied by water during the formation process of pebbles. Only a handful of lithium carbonate particles were observed in backscattered electron image in spite of the content of lithium carbonate was as high as 9.5 wt%. As part of lithium carbonate can dissolve in water, very tiny grain of lithium carbonate would precipitate during dry process. This part of lithium carbonate cannot be easily observed in the electron microscope images. Thus, green pebbles with uniform structure and composition can be obtained by graphite bed method.

3.2. Thermal treatment and phase evolution

The green pebbles were characterized by TG–DTA to determine the mass changes and sintering temperature. Fig. 3 shows the TG–DTA curves of the green pebbles during the thermal treatment process. The DTA curve indicated that an endothermic process took

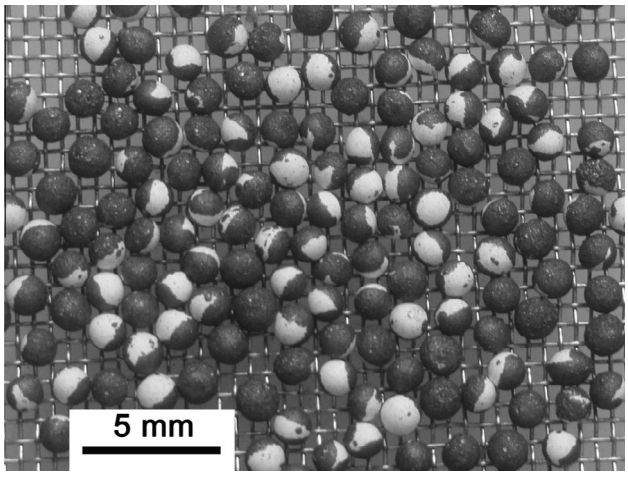

Fig. 1. Morphology of the green pebbles reprocessed by graphite bed method.