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ScienceDirect
Journal of Nuclear Materials 373 (2008) 206–211
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Optimization of a wet chemistry method for fabrication of Li_2TiO_3 pebbles

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Received 21 November 2006; accepted 24 May 2007

Abstract

Li_2TiO_3 is one of the most promising candidates for solid breeder materials. Li_2TiO_3 pebbles with about 1.20 mm in diameter and 91%T.D. were successfully prepared by an optimized wet chemistry method using citric acid as chelating agent. Thermal analysis, phase analysis and morphological observations were carried out systematically. The experimental results showed that the amount of the chelating agent influenced obviously the sphericity of the pebbles. The prepared pebbles displayed a homogeneous and temperature sensitive microstructure with an average grain size less than 3 μm while sintered at 1050 °C for 6 h.

1. Introduction

Lithium-based ceramics, such as Li_2O,Li_2ZrO_3, Li_2TiO_3, Li_4SiO_4 etc. were recognized as candidates for tritium breeding materials in fusion reactors [1,2]. Among them, lithium titanate (Li_2TiO_3) is considered to be one of the most promising candidates because of its reasonable lithium atom density, low activation, high chemical stability, good compatibility with structural materials and excellent tritium release characteristics at low temperatures [3–6].

The pebble configuration has been adopted as the preferred option for tritium breeders in the assembly of blankets with complex geometry and with regard to thermal stress and irradiation cracking [7]. Many techniques can be used to fabricate lithium titanate pebbles, e.g. solid-state reaction-based techniques involving the extrusion–spheronization–sintering process, agglomeration–sintering process and rotating granulation and wet processes such as the sol–gel method, soft chemistry method etc [8–11].

Usually, high amounts of binders must be used in the process of pebble fabrication by solid-state reaction techniques. The combustion of the binders during sintering of the pebbles would generate a lot of gas which prohibited the densification of the pebbles and led to unsatisfied density. The wet process such as the sol–gel method, soft chemistry method etc. received particular attention since no binder was used for the process and high density was therefore easily realized. Moreover, it is convenient to realize mass production by such methods, and it is advantageous from the viewpoint of reprocessing lithium-bearing solutions.

Tsuchiya et al. have studied the preparation of Li_2TiO_3 pebbles by the direct-wet process with H_2O_2 as the solvent. Although gel spheres with favorable sphericity could be fabricated when the mixed solution of 30% H_2O_2 and citric acid ($C_6H_8O_7$) was used as the solvent, it is difficult to produce dense pebbles by the post-sintering of the gel spheres [12]. In this paper, by optimizing the process parameters, Li_2TiO_3 pebbles with density as high as 91%T.D. were produced by the wet chemistry method based on 30% H_2O_2 + citric acid ($C_6H_8O_7$) solvent, influence of citric acid ratio of the solvent, handling temperature etc. on the quality of the pebbles was systematically investigated.

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0022-3115/$ - see front matter
doi:10.1016/j.jnucmat.2007.05.045

2. Experiments

2.1. Preparation of the Li_2TiO_3 powder

Precursor Li_2TiO_3 powder was synthesized by the solid state reaction technique at 700 °C for four hours based on the following chemical reaction:

$$Li_2CO_3 + TiO_2 \rightarrow Li_2TiO_3 + CO_2 \uparrow$$

Appropriate amounts of Li_2CO_3 (A.R.) and TiO_2 (A.R.) powders corresponding to the Li/Ti atomic ratio of 2 in the final ceramic products were blended by planetary ball milling for 4 h with ethyl alcohol as the milling medium. Li_2TiO_3 powders were formed by calcining the dried precursors at 700 °C for 4 h in air atmosphere.

2.2. Fabrication of Li_2TiO_3 pebbles

Fig. 1 shows the flow chart of the process for pebble preparation. A 30 wt% aqueous solution of H_2O_2 was selected as the solvent for dissolving Li_2TiO_3, and citric acid ($C_6H_8O_7$) was used as the chelating agent. The solution was heated at 60 °C in an oil bath. The reaction was highly exothermic with a lot of foam appeared. During the heating treatment, the color of the solution firstly changed to orange-red, the heating lasted until the Li_2TiO_3 content of the solution reached 25 wt%. Then the concentrated liquid was dropped into the gelation bath with acetone as the gelating agent to form gel spheres. Subsequent aging was processed at ambient temperature for sufficient time. Then the gel spheres were dried at 50 °C in air. Finally, the loose pebbles were sintered at 1050 °C for 6 h in air atmosphere.

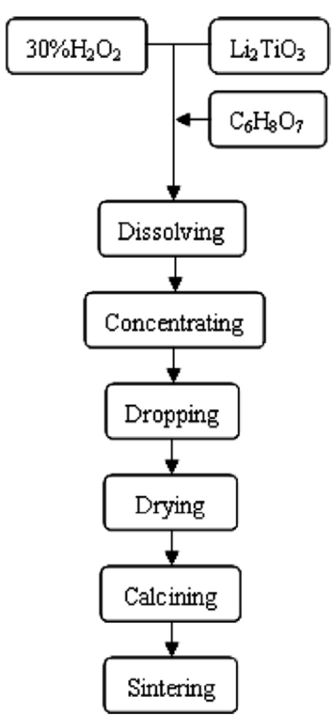

Fig. 1. Flow chart of the optimized wet chemistry method.

2.3. Characterizations

Thermal analysis of the gel spheres was performed by thermogravimetry and differential analysis (NETZSCH, STA 409 PC) in air atmospheres at a heating rate of 10 °C /min the temperature range between room temperature and 800 °C. The density of the Li_2TiO_3 pebbles was measured by Archimedes' principle using ethyl alcohol as the medium. The crystalline phases were identified by X-ray diffraction analysis (Rigaku RAD-C, 12KW) at room temperature using Cu Kα radiation, and the surface microstructure of the sintered pebbles was observed by scanning electron microscopy (EPMA-8705QH$_2$).

3. Results and discussion

3.1. Pebbles characteristics

Fig. 2 shows the morphology of a batch of Li_2TiO_3 pebble. As seen, the shape of Li_2TiO_3 pebbles was nearly spherical with the sphericity, denoted as the ratio of the maximum diameter/minimum diameter [13], of about 1.05. The diameter of the pebbles was measured by sieve classification method and distributed in the range of 1.09–1.32 mm. The average diameter of the pebbles was about 1.20 ± 0.03 mm. The density of the pebbles was measured at room temperature. A small batch of pebbles (about 50 pebbles) was tested together with the measurement of the density. When the citric acid/Li_2TiO_3 molar ratio was fixed at 1, the pebbles sintered at 1050 °C for 6 h reached an average density as high as 91%T.D.

3.2. The thermal treatment process

The sample with 18.8 mg in weight was used in the thermal treatment. Fig. 3 shows the TG/DTA profile of the gel precursor, four peaks at 125 °C, 180 °C, 370 °C and 495 °C, respectively, were observed on the DTA curve. The endothermic peak at 125 °C was ascribed to the evaporation of absorbing H_2O, the corresponding weight loss about 12% was found. Decomposition of H_2O_2 gave rise

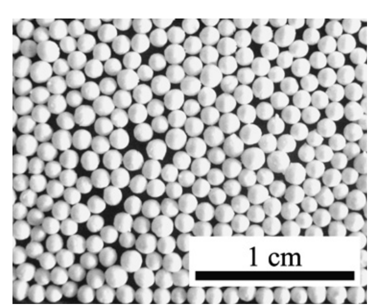

Fig. 2. The photograph of Li_2TiO_3 pebbles.