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Development of wet process with substitution reaction for the mass production of Li_2TiO_3 pebbles

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Abstract

Recently, lithium titanate (Li_2TiO_3) has attracted the attention of many researchers from the point of good tritium recovery at low temperature, chemical stability, etc. As the shape of Li_2TiO_3, a small pebble was selected as the Japanese design for a fusion reactor blanket. On the other hand, as the fabrication method of Li_2TiO_3 pebbles, the wet process is the most advantageous from the viewpoint of mass production, etc. In this study, fabrication of small Li_2TiO_3 pebbles less than ∅0.5 mm was performed by the wet process with substitution reaction, and the characteristics of Li_2TiO_3 pebbles fabricated by this process were evaluated. From the results of the fabrication tests, excellent prospects were obtained concerning mass production of Li_2TiO_3 pebbles with the target density (80–85% T.D.) and target diameter (less than ∅0.5 mm). © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

In the development of tritium breeding blankets for fusion reactors, lithium-containing ceramics such as Li_2O, Li_2ZrO_3 and Li_4SiO_4 were recognized as promising tritium breeding materials [1]. On the other hand, lithium titanate (Li_2TiO_3) has attracted the attention of many researchers from a point of easy tritium recovery at low temperature, high chemical stability, etc. [2,3]. The application of small Li_2TiO_3 pebbles was proposed in the Japanese design of a fusion reactor blanket in order to reduce thermal stress, etc. [4–7]. The wet process and sol–gel methods [8,9] are most advantageous from the viewpoint of mass production, reprocessing lithium-bearing solution and so on. In a previous paper, the fabrication of Li_2TiO_3 pebbles by a wet process with dehydration reaction was reported [10].

In this study, fabrication of small Li_2TiO_3 pebbles less than ∅0.5 mm was performed by a wet process with substitution reaction, and characteristics of the Li_2TiO_3 pebbles fabricated by this process were evaluated.

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2. Experimental

2.1. Materials

Li_2TiO_3 powder, fabricated by Soekawa Chemical, was prepared with a purity of 99.9%. The particle size of the Li_2TiO_3 powder was in the range of 0.2–2.3 and 0.63 μm on an average. Sodium alginate and tetrahydrofurfuryl alcohol (4HF) fabricated by Wako Pure Chemical Industries were used as the binder and plasticizer, respectively. Zinc chloride with a purity of 96% was prepared as the gelling agent.

2.2. Fabrication process

The wet process with substitution reaction is as follows:

1. *Fabrication of gel-spheres*: A liquid mixture of Li_2TiO_3 powder and sodium alginate solution as the binder is dropped in zinc chloride through a nozzle, and gel-spheres are generated.
2. *Calcination of gel-spheres*: Zinc in the gel-spheres is removed in a hydrogen gas atmosphere, and Li_2TiO_3 spheres with low density are obtained.
3. *Sintering*: The Li_2TiO_3 spheres are sintered in air, and Li_2TiO_3 pebbles with high density are fabricated.

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The flow chart of the fabrication process of Li_2TiO_3 pebbles by this wet process with substitution reaction and the most important fabrication parameters are shown in Fig. 1.

A schematic drawing of the automatic dropping system for mass production is shown in Fig. 2. This system consists of a liquid mixture tank, vibration generator, nozzle for dropping and zinc chloride solution tank for aging. The diameter of droplets is generally given as follows:

$$D = \left(\frac{6Q}{\pi f}\right)^{1/3}, \qquad (1)$$

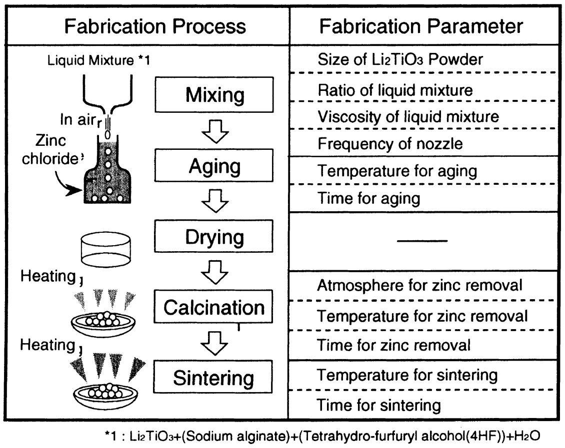

Fig. 1. Flow chart of fabrication process of Li_2TiO_3 pebbles by wet process with substitution reaction and the most important fabrication parameters.

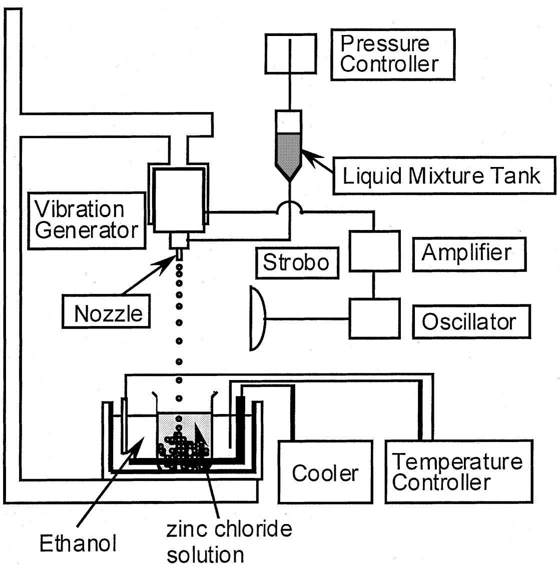

Fig. 2. Schematic drawing of automatic dropping system for mass production.

where D (cm) is the diameter, Q (cm^3/s) the flow rate of liquid mixture, and f (Hz) is the frequency of nozzle. The frequency of the vibration generator is given by the oscillator. The diameter of the droplets is also influenced by the viscosity of the liquid mixture, the nozzle diameter, and wettability between the material of nozzle and liquid mixture. Additionally, the sphericity is influenced by the viscosity of liquid mixture and the frequency of nozzle.

2.3. Parameter survey tests

In the parameter survey tests, the mixing ratio of Li_2TiO_3 powder, the binder (sodium alginate) and the plasticizer (4HF), and the frequency of vibration of the nozzle were examined for the fabrication of Li_2TiO_3 pebbles with small diameter and high sphericity. A removal test of zinc from the gel-spheres was also conducted in the temperature range from 800°C to 1000°C for 4 h in hydrogen gas atmosphere.

Additionally, the effect of sintering temperature on grain size of the Li_2TiO_3 pebbles was examined.

2.4. Characterization method of Li_2TiO_3 pebbles

The Li_2TiO_3 pebbles fabricated in the preliminary fabrication test were characterized by the following. Density of Li_2TiO_3 pebbles was measured by mercury porosimetry. Microstructure and crystal form were measured with a scanning electron microscope (SEM) and an X-ray diffractometer (XRD), respectively. The collapse loads were measured with an unconfined compression tester with the compression indenter made of SiC. Impurities in the Li_2TiO_3 pebbles were measured with an atomic emission spectrometer with inductively coupled plasma (ICP-AES) and an atomic absorption spectorometer (AAS).

3. Results and discussion

3.1. Parameter survey tests

In the first experiment, the mixing ratio of Li_2TiO_3 powder, the binder (sodium alginate) and the plasticizer (4HF) were decided for the fabrication of gel-spheres with high sphericity. When the concentration of sodium alginate was less than 0.5 wt%, the liquid mixture of sodium alginate and 4HF solution gelled in zinc chloride, but the gel-spheres sphericity was not high. On the other hand, when the content of 4HF was high, the liquid mixture gelled during the mixing process. From this experiment, gel-spheres with high sphericity were fabricated when the concentrations of sodium alginate and 4HF were 1.0 and 20 wt%, respectively.

In the second experiment, Li_2TiO_3 powder was added in the liquid mixture of sodium alginate and 4HF solution and each mixture was dropped into zinc chloride. The relationship between the content of Li_2TiO_3 powder and the diameter/sphericity of gel-spheres is shown in Fig. 3. In this test, the frequency of vibration of the nozzle was 80 Hz. From this result, the diameter of gel-spheres increased with increasing content of Li_2TiO_3 powder. It became clear that the diameter of gel-spheres also depended on the nozzle diameter. Sphericity of gel-spheres, which is the ratio of the longest diameter to the shortest diameter, was less than 1.15 and better in the range of this experimental parameter.

In the third experiment, the dependence on the frequency of nozzle vibration of the sphericity of gel-spheres was estimated. The frequency of nozzle vibration was changed from 80 to 1000 Hz. When the frequency of nozzle vibration was from 80 to 250 Hz, gel-spheres sphericity was high and the diameter of gel-sphere was almost constant in each condition. On the other hand, when the frequency of nozzle vibration was more than 500 Hz, gel-spheres sphericity was not high. From this experiment, the frequency of nozzle vibration was selected less than 250 Hz.

In the fourth experiment, the effect of sintering temperature on grain size of the Li_2TiO_3 pebbles was examined. SEM photographs of Li_2TiO_3 pebbles at each sintering temperature are shown in Fig. 4. At a sintering condition of 950°C for 4 h, Li_2TiO_3 pebble density was about 71% T.D. with a grain size of about 1.0 μm. The microstructure of the Li_2TiO_3 pebbles was altered and grain coarsening was seen. Typical sintering phenomena such as neck growth, particle coalescence, and pore growth were observed in the microstructure. The sintering temperatures above 1150°C yielded completely different microstructural features. The grains cannot be distinguished in the fracture surface. They grew extensively (over 20 μm) with no remnants of the initial boundaries. The Li_2TiO_3 pebble density was more than 90% T.D.

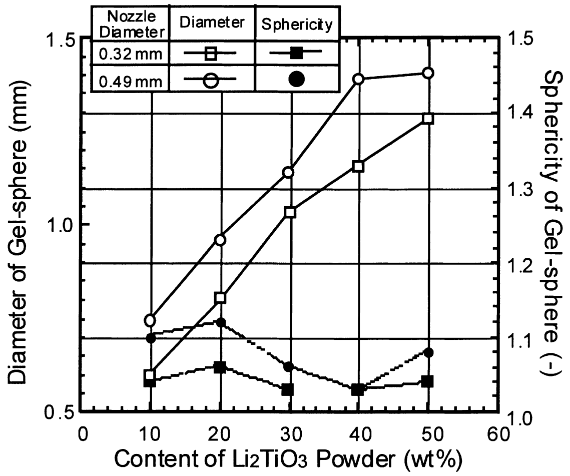

Fig. 3. Relationship between content of Li_2TiO_3 powder and diameter/sphericity of gel-spheres.

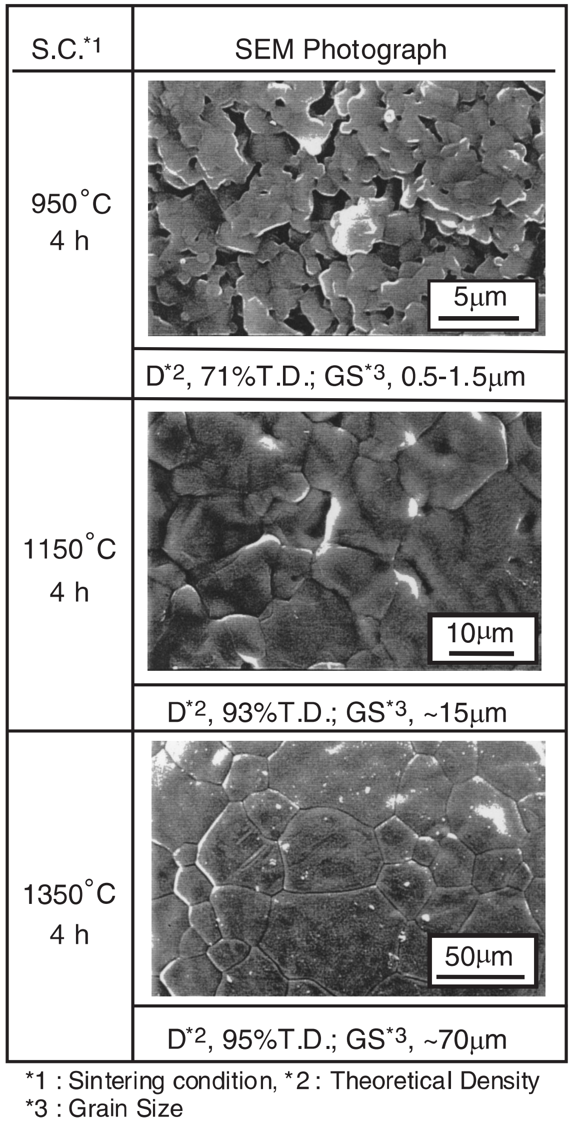

Fig. 4. SEM photograph of Li_2TiO_3 pebbles at each sintering temperature.

3.2. Characterization of Li_2TiO_3 pebbles

A summary on the characteristics of Li_2TiO_3 pebbles is shown in Table 1. The main features are discussed below.

The distributions on diameter and sphericity of Li_2TiO_3 pebbles fabricated in this study are shown in Figs. 5 and 6, respectively. The size of the Li_2TiO_3

Table 1
Characteristics of Li_2TiO_3 pebbles

Properties	Measuring method	Measuring values
Density	Liquid immersion method (Hg)	88.7% T.D.
Sphericity	Photographic analysis	1.21
Pebble diameter	Sieve classification	0.238 mm
Crystal structure	XRD analysis	Li_2TiO_3, $Li_{1.33}Ti_{1.66}O_4$
Impurity content	ICP analysis, etc.	Na, 58; Mg, 4; Ca, 15; Si, 170; Fe, 13 (in ppm) Zn, 1.5 (in %)
Collapse load	Autograph	0.26 kgf

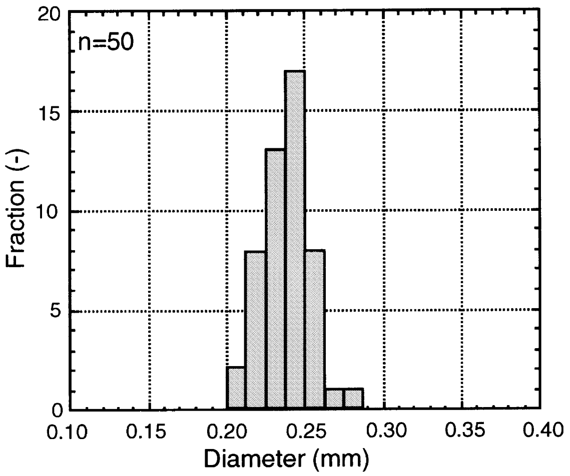

Fig. 5. Distribution of diameter of Li_2TiO_3 pebbles fabricated in the preliminary fabrication test.

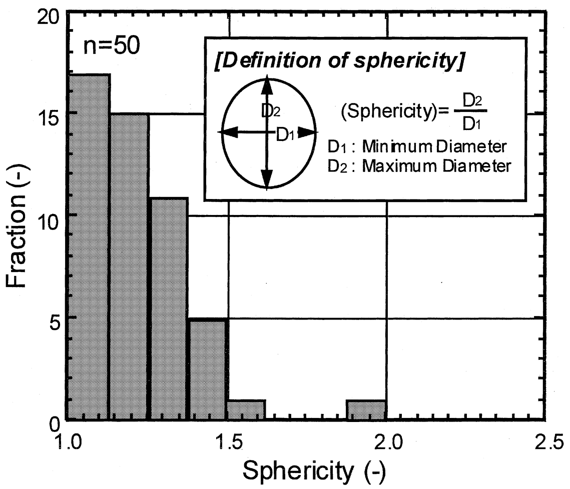

Fig. 6. Distribution of sphericity of Li_2TiO_3 pebbles fabricated in the preliminary fabrication test.

pebbles was 0.238 ± 0.014 mm (av.). Sphericity of Li_2TiO_3 pebbles was measured by the photographic analysis method, and it was a very high value of 1.21 ± 0.18. The crystal form of the Li_2TiO_3 pebbles was observed by XRD, and only X-ray peaks of Li_2TiO_3 and $Li_{1.33}Ti_{1.66}O_4$ were detected. The impurities in the Li_2TiO_3 pebbles were as follows: Na, 58; Ca, 15; Mg, 4; Al, 25; Si, 170; Zn, 1.3×10^4 (in ppm). From this analysis, it is shown that impurities except for Zn were not mixed in Li_2TiO_3 pebbles by this process and survey tests should be carried out to determine the condition for zinc removal.

4. Conclusion

Fabrication tests for mass production and characterization of small Li_2TiO_3 pebbles were carried out by the wet process with substitution reaction. The following can be concluded:

1. For the stable fabrication of gel-spheres, sodium alginate concentration of 1.0 wt% and 4HF concentration of 20 wt% were selected as the optimum conditions. The content of Li_2TiO_3 powder and the frequency of nozzle vibration were decided by Li_2TiO_3 pebble diameter.
2. As for the shape of the Li_2TiO_3 pebbles fabricated in the optimum condition, the diameter was about 0.23 mm and the sphericity was less than 1.2. However, survey tests should be carried out to determine the condition for zinc removal.

From these tests, the mass production of Li_2TiO_3 pebbles by the wet process with substitution reaction looks promising.

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