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Fabrication development and preliminary characterization of Li_2TiO_3 pebbles by wet process

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Abstract

Lithium titanate (Li_2TiO_3) has attracted attention of many researchers because of easy tritium recovery at low temperature, high chemical stability, etc. The application of small Li_2TiO_3 spheres has been proposed in some designs of fusion blanket. Although, the wet process and sol–gel method are the most advantageous as a fabrication method of Li_2TiO_3 pebbles from points of mass production, and of reprocessing necessary for effective use of resources and reduction of radioactive wastes. However, the fabrication of Li_2TiO_3 pebbles by the wet process has not been established. Therefore, in this study, fabrication development and preliminary characterization of Li_2TiO_3 pebbles by the wet process were performed, noting the aging and sintering conditions in the fabrication process of gel-spheres. At the best condition, Li_2TiO_3 pebbles with the target density of 80–85%T.D. were obtained.

1. Introduction

In the development of tritium breeding blankets for fusion reactors, lithium-containing ceramics such as Li_2O, $LiAlO_2$, Li_2ZrO_3, Li_2TiO_3 and Li_4SiO_4 were quickly recognized as promising tritium breeding materials[1,2].

Particularly, lithium titanate (Li_2TiO_3) has attracted an attention of many researchers because of easy tritium recovery at low temperature, high chemical stability [3–5] etc. The application of small Li_2TiO_3 pebbles was proposed in Japanese design of fusion blanket in order to reduce thermal stress, etc. [6–9]. Recently, reprocessing technology on irradiated ceramic tritium breeders was developed from a point of effective use of resources and reduction of radioactive wastes [10,11]. The wet process and sol–gel method [12–15] are the most advantageous for fabricating small Li_2TiO_3 pebbles from the reprocessing lithium-bearing solution. However, no fabrication of Li_2TiO_3 pebbles has been established by the wet process.

In this study, fabrication tests of Li_2TiO_3 pebbles were carried out by the wet process and the characteristics of the Li_2TiO_3 pebbles were evaluated. Especially, aging condition and sintering condition were optimized in order to raise density of Li_2TiO_3 pebbles by the wet process.

2. Experimental

2.1. Materials

Li_2TiO_3 powder was prepared with purity of 99.9%. This powder was manufactured by Cerac. The main impurities of the Li_2TiO_3 powder were as follows: Na, 95; Ca, 140; Mg, 39; Al, 130; Si, 190; Co, 3; B<25 (in ppm). The particle size of the Li_2TiO_3 powder was in the region of 0.3–70 and 10 μm on an average. Polyvinylalcohol (PVA), manufactured by Kuraray, was used as the binder of the Li_2TiO_3 powder.

2.2. Fabrication process

The most important feature of the wet process is that Li_2TiO_3 powder is used as the starting material to

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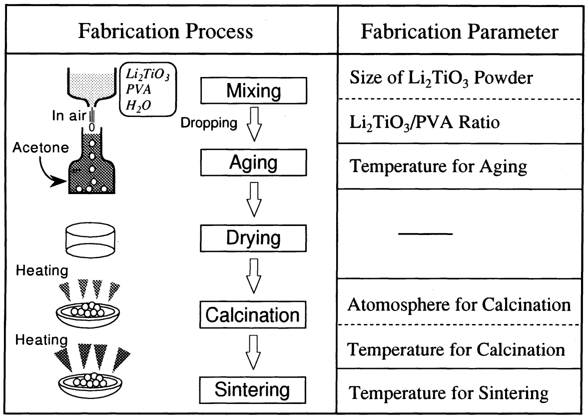

Fig. 1. Flow chart of fabrication process of Li_2TiO_3 pebbles and fabrication parameter for increasing Li_2TiO_3 pebble density.

produce Li_2TiO_3 pebbles. A flow chart of fabrication process of Li_2TiO_3 pebbles and the most important fabrication parameters for increasing Li_2TiO_3 pebble density are shown in Fig. 1. The process is shown as follows.

1. *Fabrication of gel-spheres*. A liquid mixture of Li_2TiO_3 and PVA solution is dropped in cooled acetone through a nozzle, and gel-spheres are fabricated.
2. *Calcination of gel-spheres*. PVA in the gel-spheres is removed, and low density Li_2TiO_3 spheres are fabricated.
3. *Sintering*. The Li_2TiO_3 spheres are sintered in air, and high density Li_2TiO_3 pebbles are fabricated.

2.3. Fabrication tests

In the first fabrication test, gel-spheres were fabricated under the mixing condition of Li_2TiO_3 (43 wt%), PVA (4 wt%) and water (53 wt%). The gel-spheres were calcinated and sintered, and then the characteristics of the Li_2TiO_3 pebbles, i.e. density, sphericity, etc., were evaluated.

In the second fabrication test, dropping test of gel-spheres was carried out to decide the optimum mixing ratio of Li_2TiO_3 powder and PVA solution. Sintering conditions (temperature and time for sintering) were changed.

In the third fabrication test, the aging condition was changed and the relationship between the aging temperature and the cracking ratio, i.e. the number ratio of cracked gel-spheres to all the gel-spheres, was evaluated. The gel-spheres were heated at 650°C for 6 h in air and sintered at 1400°C for 4 h.

In the fourth fabrication test, sintering test was conducted in the sintering temperature range from 1100°C to 1430°C for 4 h in air. The aging condition was selected to be −30°C for 1 h.

2.4. Characterization method of Li_2TiO_3 pebbles

The Li_2TiO_3 pebbles 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. The impurities in Li_2TiO_3 pebbles were measured with an atomic emission spectrometer with inductively coupled plasma (ICP-AES) and an atomic absorption spectrometer (AAS), and the carbon content in the Li_2TiO_3 pebbles was measured by the infrared absorptiometric method.

3. Results and discussions

3.1. Optimization on fabrication method of Li_2TiO_3 pebbles

Optimized conditions obtained by each fabrication test of Li_2TiO_3 pebbles are shown in Table 1. Fabrication tests were conducted four times. From the results obtained in these tests, the optimization of the fabrication method is discussed as follows in detail.

3.1.1. Li_2TiO_3/PVA ratios

In the first fabrication test, the density of the Li_2TiO_3 pebbles was 40%T.D. Therefore, fabrication tests were additionally performed three times in order to raise the sintering density of the Li_2TiO_3 pebbles fabricated by the wet process.

In the second fabrication test, the fabrication of gel-spheres was performed under various mixing ratios between Li_2TiO_3 powder and PVA solution. The relationship between the contents of PVA solution and

Table 1
Optimized conditions obtained by each fabrication test of Li_2TiO_3 pebbles

Fabrication test	Process					Density
	Mixture ratio	Aging temperature	Calcination condition	Sintering time	Sintering temperature	
First test	Li_2TiO_3:43 wt% PVA:4 wt%	0°C	650°C 6 h	10 h	1000°C	40%T.D.
Second test	Li_2TiO_3:46 wt% PVA:4 wt%	0°C	650°C 6 h	4 h	1150°C	60%T.D.
Third test	Li_2TiO_3:46 wt% PVA:4 wt%	−20°C	650°C 6 h	4 h	1400°C	76%T.D.
Fourth test	Li_2TiO_3:46 wt% PVA:4 wt%	−30°C	650°C 6 h	4 h	1400°C	81%T.D.

Remark: The aging temperature and sintering temperature were effective to increase the density of Li_2TiO_3 pebbles.

Li_2TiO_3 powder for gel-sphere fabrication is shown in Fig. 2. The shape of the gel-spheres in region A, with the Li_2TiO_3 to PVA ratios of e.g. 62 and 3 wt% was not sphere. In this region, the viscosity of the liquid mixture was too high because of high content of Li_2TiO_3 powder. Therefore, the liquid mixture was difficult to leave from the nozzle. On the other hand, the shapes of gel-sphere in region B and C, where the Li_2TiO_3/PVA ratios were 46/4 wt% and 47/3 wt%, respectively, were almost spherical. Especially, the gel-spheres in region B had high sphericity. From these results, the Li_2TiO_3 and PVA ratio of the region B was chosen as the optimum condition. The sphericity of the gel-spheres fabricated from the pulverized Li_2TiO_3 powder were better than that of the gel-spheres fabricated from Li_2TiO_3 powder before pulverization. The gel-spheres were heated at 650°C for 6 h in air and sintered at 1150°C for 4 h. In this experiment, the density of Li_2TiO_3 pebbles was 60%T.D.

3.1.2. Aging condition

Aging temperature dependence on the content density of Li_2TiO_3 in the gel-spheres and on the cracking ratio of the gel-spheres is shown in Fig. 3. The aging time was selected to be 1 h. In Fig. 3, the Li_2TiO_3 content in the gel-spheres increased with decreasing aging

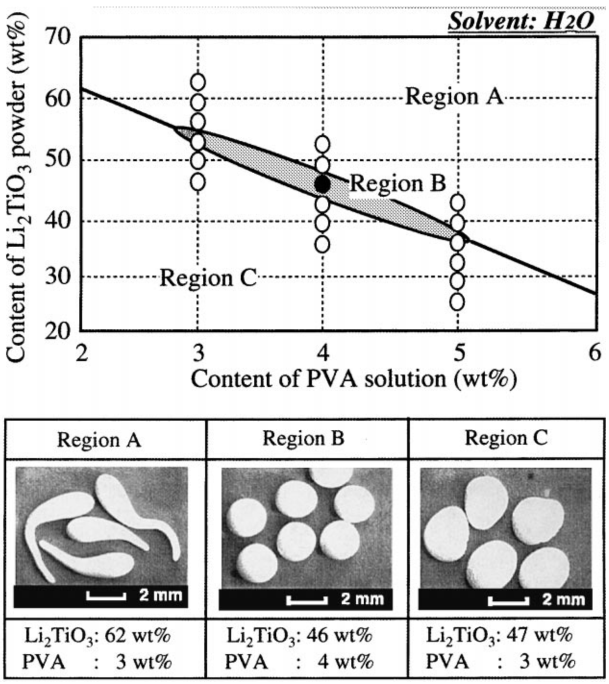

Fig. 2. Relationship between content of PVA solution and content of Li_2TiO_3 powder for gel-spheres fabrication.

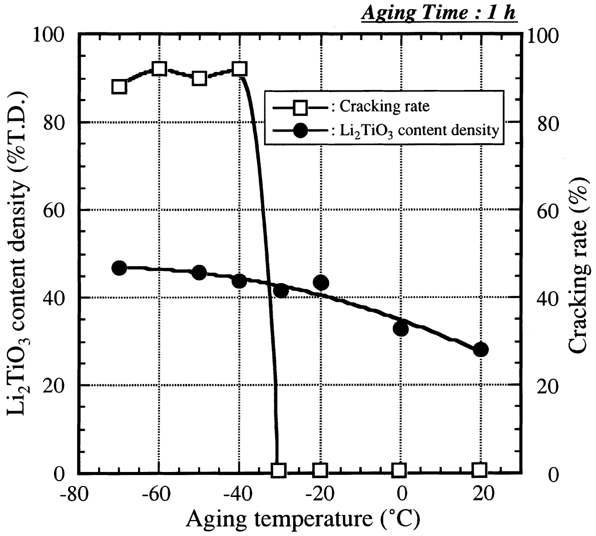

Fig. 3. Aging temperature dependence on content density of Li_2TiO_3 in gel-spheres and on cracking rate of gel-spheres.

temperature. It seems that the contraction of gel-spheres increased with decreasing aging temperature.

On the other hand, gelation of PVA solution occurs at less than −10°C in air. In this test, the gelation of the liquid mixture occurred at less than 0°C in acetone. It seems that the dehyrdration of the gel-spheres was hastened by acetone. However, when the aging temperature was lower than −40°C, the cracking ratio of the gel-spheres was more than 90%. It can be considered that the freezing point of the liquid mixture affects the cracking rate of the gel-spheres.

From the evaluation results of aging temperature, the aging condition was selected to be between −20°C and −30°C for 1 h. The gel-spheres were heated at 650°C for 6 h and sintered at 1400°C for 4 h. In this test, the density of Li_2TiO_3 pebbles was 76%T.D.

3.1.3. Sintering condition

Relationship between sintering temperature and Li_2TiO_3 pebble density is shown in Fig. 4. At a sintering condition of 1000°C for 4 h, Li_2TiO_3 pebble density was 54%T.D. with a grain size of about 4 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. At a sintering condition of 1200°C for 4 h, Li_2TiO_3 pebble density was 64%T.D. with a grain size of about 10 μm. The microstructure showed further evidence of sintering such as grain growth and decreasing number of pore with larger size. Particles bridged by necks, are well bonded together by diffusion. The sintering temperatures above 1400°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 80%T.D.

The grain size and density of Li_2TiO_3 pebbles increased with increasing sintering temperature. The extent of grain coarsening and achievable final density depend on the rate-controlling mechanism in the coarsening and densification kinetics.

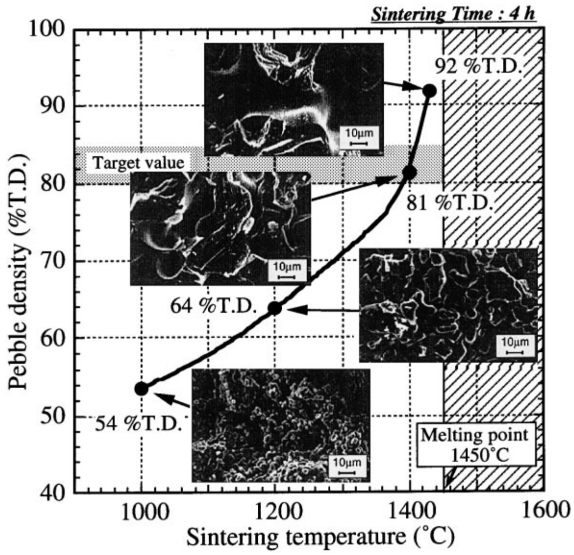

Fig. 4. Relationship between sintering temperature and Li_2TiO_3 pebble density.

Table 2
Summary on specification of Li_2TiO_3 pebbles

Properties	Measuring methods	Measuring values
Density	Liquid immersion method (Hg)	81.3%T.D.
Sphericity	Photographic analysis	1.11 (av.)
Pebble diameter	Sieve classification	1.52 mm (av.)
Grain size	SEM observation	50 μm (av.)
Crystal structure	XRD analysis	XRD Pattern
Impurity content	ICP analysis	Na, 120; Ca, 150; Si, 170; Al, 140; Mg, 33 (in ppm)
Collapse load	Autograph	46.1 N (av.)

3.2. Characterization of Li_2TiO_3 pebbles

The characterization of the Li_2TiO_3 pebbles fabricated in the fourth fabrication test was carried out. Summary on the specification of the Li_2TiO_3 pebbles is shown in Table 2. The main features are discussed below.

The density of the Li_2TiO_3 pebbles fabricated by this process was 81%T.D. The size of the Li_2TiO_3 pebbles was 1.52 ± 0.05 mm (av.). Sphericity of Li_2TiO_3 pebbles, which is the ratio of the longest diameter to the shortest diameter, was measured by the photographic analysis method, and it was a very high value of 1.11 ± 0.07. Distribution on the collapse load of Li_2TiO_3 pebbles fabricated by the wet process is shown in Fig. 5. The average collapse load was 46.1 ± 8.8 N. The crystal form of the Li_2TiO_3 pebbles was observed by XRD, and only X-ray peaks of Li_2TiO_3 were detected. The main impurities in the Li_2TiO_3 pebbles were as follows: Na, 120; Ca, 150; Mg, 33; Al, 140; Si, 170; Co, 1; B, 5; C, 48 (in ppm). From this analysis, it is shown that impurities were not mixed in Li_2TiO_3 pebbles by this process.

From the results of these tests, bright prospects were obtained concerning the fabrication of Li_2TiO_3 pebbles by the wet process.

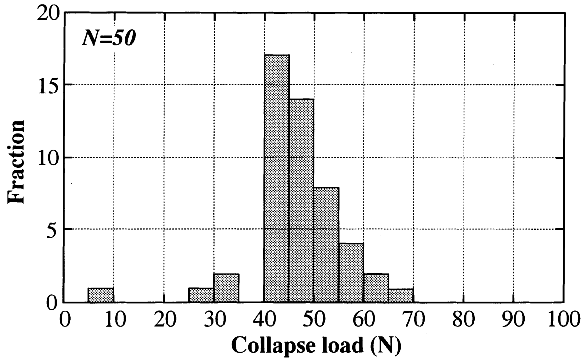

Fig. 5. Distribution on collapse load of Li_2TiO_3 pebbles fabricated in the fourth fabrication test.

4. Conclusion

Fabrication tests of small Li_2TiO_3 pebbles were carried out by the wet process and the following can be concluded.

1. It was obvious that the density of the Li_2TiO_3 pebbles was susceptible to aging temperature and sintering temperature. The aging temperature was selected to be −30°C for 1 h.
2. The grain size and density of the Li_2TiO_3 pebbles increased with increasing sintering temperature. The extent of grain coarsening and the achievable final density depend on the rate-controlling mechanism in the coarsening and densification kinetics.
3. When the gel-spheres obtained in the fourth fabrication test were heated at 650°C for 6 h and sintered at 1400°C for 4 h, the density of Li_2TiO_3 pebbles was raised up to the target values. As the shape of the Li_2TiO_3 pebbles, the diameter was 1.5 mm and the sphericity was resulted less than 1.2.

From these tests, bright prospects were obtained concerning the fabrication process of Li_2TiO_3 pebbles by the wet process. In the future plan, an automatic-control dropping system of gel-spheres will be designed and developed for mass production.

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