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Control of particle size and density of Li_2TiO_3 pebbles fabricated by indirect wet processes

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Abstract

A small pebble has been selected as the shape of lithium titanate (Li_2TiO_3) in the Japanese design of the fusion blanket. In the present study, fabrication tests of Li_2TiO_3 pebbles were carried out by two kinds of indirect wet processes (a wet process using a dehydration reaction and another wet process using a substitution reaction), and the basic characteristics of each kind of Li_2TiO_3 pebbles were evaluated for irradiation tests with the Japan Materials Testing Reactor (JMTR). From results of the fabrication tests and characterization, bright prospects were obtained concerning mass production of Li_2TiO_3 pebbles with a target diameter of 0.2–2.0 mm and a target density of 80–85% theoretical density (TD) by these two kinds of indirect wet processes.

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 recognized as promising tritium breeders [1,2]. Recently, lithium titanate (Li_2TiO_3) has attracted attention of many researchers from viewpoints of good tritium recovery at low temperature, chemical stability, low tritium inventory and other good properties [3–6].

A small pebble has been selected as the shape of Li_2TiO_3 in the Japanese design of the fusion blanket [7–9]. Fabrication tests of Li_2TiO_3 pebbles have been performed by various methods such as a rotating granulation method, an extrude/tumble method and wet processes [10–15]. The wet process is the most advantageous as the fabrication method of Li_2TiO_3 pebbles from viewpoints of mass fabrication and lithium recycling. Additionally, a packing method of two-component pebbles has been proposed for high thermal conductivity and high tritium breeding ratio in the design of fusion blankets [16].

In the present study, fabrication tests of Li_2TiO_3 pebbles were carried out by two kinds of indirect wet processes using a dehydration reaction [14] or a substitution reaction [15]. The latter process was devised to fabricate small Li_2TiO_3 pebbles with a diameter under 0.5 mm, which are difficult to be fabricated by the former process. The fabrication conditions were decided to meet target values (particle size, density and grain

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size), and basic characteristics of each kind of Li_2TiO_3 pebbles were evaluated for irradiation tests with the Japan Materials Testing Reactor (JMTR) of Japan Atomic Energy Research Institute (JAERI).

2. Experimental

Li_2TiO_3 powder with a purity of 99.9% was fabricated by Soekawa Chemical Co. Ltd. The particle size of the Li_2TiO_3 powder was in the range of 0.2–2.3 μm in diameter, and the average diameter was 0.63 μm diameters.

Two kinds of Li_2TiO_3 pebbles were fabricated by the indirect wet process using the dehydration reaction and the substitution reaction. The flow chart of the fabrication process of the Li_2TiO_3 pebbles is shown in Fig. 1. The basic procedure includes fabrication of Li_2TiO_3 powder, fabrication of gel-spheres, a calcination process and a sintering process.

In the first fabrication test, large pebbles were fabricated by the wet process using the dehydration reaction. Contents of Li_2TiO_3 powder, polyvinyl alcohol (PVA) and water (H_2O) in the liquid mixture were examined for fabrication of Li_2TiO_3 pebbles with high sphericity and particle size, and the nozzle diameter was selected for fabrication of Li_2TiO_3 pebbles with 2 mm diameter.

In the second fabrication test, small pebbles were fabricated by the wet process using the substitution reaction. Contents of the binder (sodium alginate), the plasticizer (tetrahydro-furfuryl alcohol (4HF)) and water (H_2O) as the solution, as well as the content of Li_2TiO_3 powder and the frequency of vibration of the nozzle of the automatic dropping system, were selected for fabrication of Li_2TiO_3 pebbles with small diameter and high sphericity. The nozzle diameter was 0.32 mm for fabrication of the small size pebbles with 0.3 mm diameter. The frequency of nozzle vibration was selected as 250 Hz from the result of the preliminary test [15]. The liquid mixture released from the nozzle was dropped into zinc chloride ($ZnCl_2$) and the gel-spheres were fabricated by the exchange reaction of Na^+ and Zn^{2+}. Therefore, a removal test of zinc (Zn) from the gel-spheres was also conducted in a temperature range from 800 to 1000 °C for 4 h in hydrogen gas atmosphere.

The effect of the sintering temperature on the density of the Li_2TiO_3 pebbles was examined at a sintering condition of 900–1350 °C in air. The Li_2TiO_3 pebbles were characterized in the following methods. The density of the Li_2TiO_3 pebbles was measured by mercury porosimetry. The microstructure was observed by scanning electron microscopy (SEM) and photographic analysis equipment, and the crystalline structure was analyzed by X-ray diffractometry (XRD). The impurities in the Li_2TiO_3 pebbles were measured by atomic emission spectrometry with an inductively coupled plasma (ICP-AES) and by atomic absorption spectrometry (AAS). The collapse loads were measured with an unconfined compression tester with a compression indenter made of SiC.

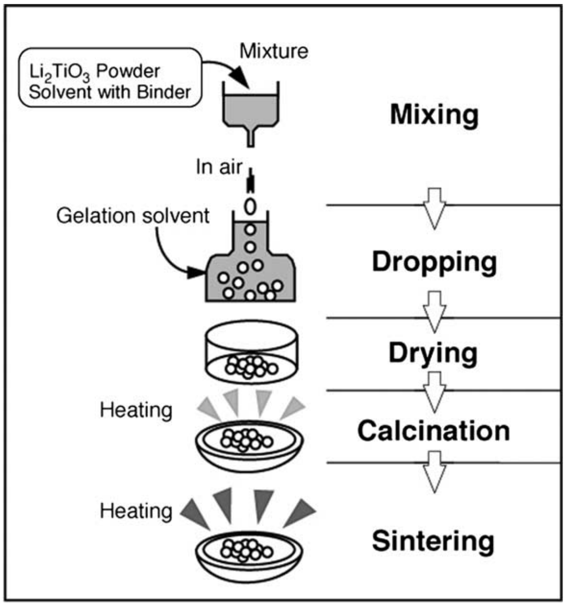

Fig. 1. Flow chart of fabrication process of Li_2TiO_3 pebbles.

3. Results and discussion

3.1. Wet process using dehydration reaction

For the large pebbles (diameter: about 2 mm), the fabrication of gel-spheres was performed with various contents of Li_2TiO_3 powder, PVA and H_2O. The aging condition of gel-spheres was selected as −30 °C for 1 h in acetone. The gel-spheres were not spherical when the contents of Li_2TiO_3 powder/PVA/H_2O were 62/3/35 wt%, respectively, in the liquid mixture. In this condition, the viscosity of the liquid mixture was high because of the high content of the Li_2TiO_3 powder. Therefore, it was difficult for the liquid mixture to leave from the tip of the nozzle. On the other hand, the shape of gel-spheres with the liquid mixture of Li_2TiO_3/PVA/H_2O in 40/4.5/55.5 wt% was almost spherical, and this content ratio was chosen as the optimum condition.

In the next step, the optimum nozzle diameter was searched for fabrication of the Li_2TiO_3 pebbles with 2 mm diameter. The relationship between the nozzle diameter and the average diameter of Li_2TiO_3 pebbles fabricated by the wet process using the dehydration reaction is shown in Fig. 2. In this figure, the diameter

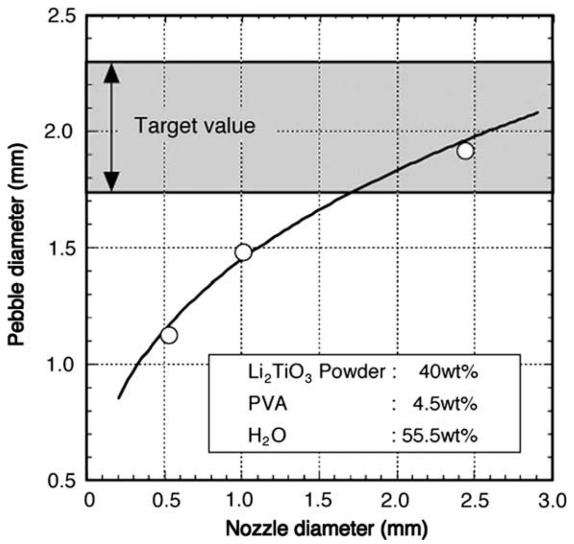

Fig. 2. Relationship between nozzle diameter and average diameter of Li_2TiO_3 pebbles fabricated by wet process using dehydration reaction.

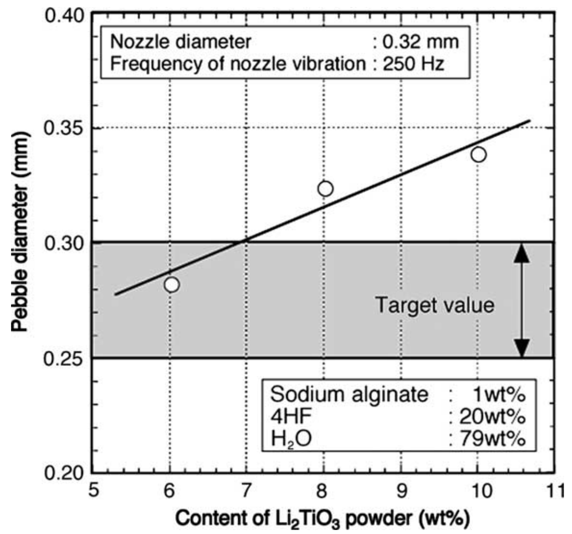

Fig. 3. Relationship between Li_2TiO_3 powder content and average diameter of Li_2TiO_3 pebbles fabricated by wet process using substitution reaction.

of Li_2TiO_3 pebbles increases with increasing the nozzle diameter.

In conclusion, it is shown in this section that the gel-spheres with the liquid mixture of $Li_2TiO_3/PVA/H_2O$ in 40/4.5/55.5 wt% were almost spherical, and that the nozzle with 2.4 mm diameter was selected for fabrication of Li_2TiO_3 pebbles with 2 mm diameter.

3.2. Wet process using substitution reaction

For the small pebbles (diameter: about 0.3 mm), the contents of sodium alginate, 4HF and H_2O were examined in the first experiment without adding Li_2TiO_3 powder for fabrication of gel-spheres with high sphericity. When the content of 4HF was appropriate, the liquid mixture gelled during the mixing process. The content of 4HF was chosen as 20 wt%. When the content of sodium alginate was less than 0.5 wt%, the liquid mixture of sodium alginate, 4HF and H_2O gelled in $ZnCl_2$, but the sphericity of gel-spheres was not good. Therefore, the contents of sodium alginate/4HF/H_2O were selected as 1/20/79 wt%, respectively, for fabrication of gel-spheres with high sphericity.

In the second experiment, Li_2TiO_3 powder was added in the mixed solution of sodium alginate, 4HF and H_2O. Fig. 3 shows the relationship between the content of Li_2TiO_3 powder and the average diameter of Li_2TiO_3 pebbles fabricated by the wet process using the substitution reaction. In this figure, the diameter of Li_2TiO_3 pebbles increases with increasing the content of Li_2TiO_3 powder.

In conclusion, it is shown in this section that the content ratio of sodium alginate/4HF/H_2O was selected as 1/20/79 wt% for the solution, and that the content of the Li_2TiO_3 powder was selected to be 5 wt% of the total solution for fabrication of Li_2TiO_3 pebbles with 0.3 mm diameter.

3.3. Sintering and characterization

The theoretical density of Li_2TiO_3 is 3.43 g/cm^3 [5] and the target density of Li_2TiO_3 pebbles is 80–85% TD. Therefore, the effect of sintering temperature on the density of two kinds of Li_2TiO_3 pebbles was examined at a sintering condition of 900–1300 °C in air. Fig. 4 shows the relationship between the sintering temperature and the density of Li_2TiO_3 pebbles fabricated by the two kinds of indirect wet processes. In this figure, the density of Li_2TiO_3 pebbles increases with increasing sintering temperature. From this result, a sintering temperature of 1180–1280 °C was selected for fabrication of Li_2TiO_3 pebbles with the target density in the wet process by the dehydration reaction. On the other hand, a sintering temperature of 1120–1220 °C was selected in the wet process using the substitution reaction for fabrication of Li_2TiO_3 pebbles with the same target density.

Results of characterization of the two kinds of Li_2TiO_3 pebbles fabricated under the above-described conditions are summarized in Table 1. The main features are discussed below. The diameter distribution of two kinds of Li_2TiO_3 pebbles is shown in Fig. 5. The average diameters of the large and small Li_2TiO_3 pebbles were about 1.9 and 0.27 mm, respectively. The degrees of sphericity (defined as the ratio of the largest diameter to the smallest diameter of each pebble) were as large

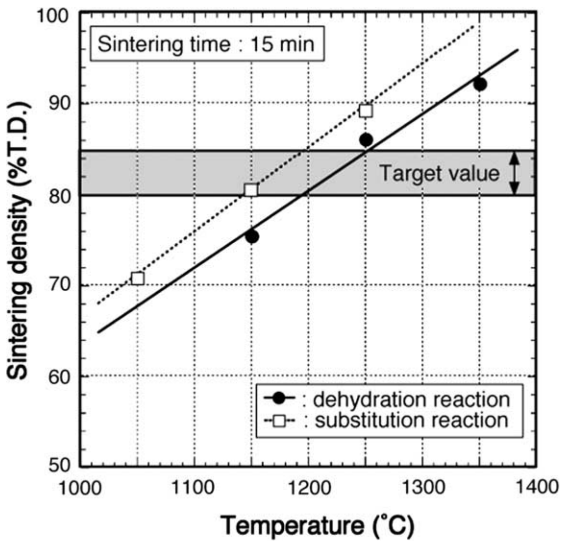

Fig. 4. Relationship between sintering temperature and density of Li_2TiO_3 pebbles fabricated by indirect wet processes.

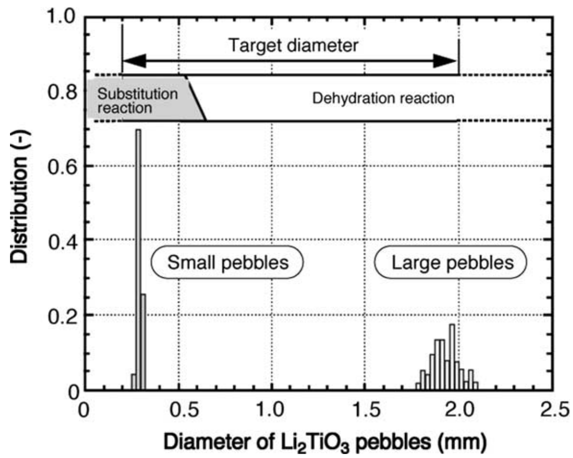

Fig. 5. Diameter distribution of two kinds of Li_2TiO_3 pebbles fabricated by indirect wet process using substitution or dehydration reactions.

as 1.05–1.1. The SEM and analytical photographs of the large and small Li_2TiO_3 pebbles are shown in Fig. 6. The average grain sizes of the large and small Li_2TiO_3 pebbles were 1.9 and 4.3 μm, respectively, which are satisfactory values.

The average densities of the large and small Li_2TiO_3 pebbles were 2.86 and 2.82 g/cm^3, respectively. Results of impurity analysis of these Li_2TiO_3 pebbles are shown in Table 2. Silicon (Si), sodium (Na) and carbon (C) were the highest impurities detected in the large pebbles. On the other hand, aluminum (Al), silicon (Si), sodium (Na) and iron (Fe) were the highest impurities detected in the small pebbles. The average crushing load of the large and small pebbles was about 73 and 4.6 N, respectively. Only X-ray peaks corresponding to Li_2TiO_3 (JCPDS card: 33-0831) were detected in XRD analysis for pebbles fabricated and packed in a polyethylene sheet.

In conclusion, the large and small Li_2TiO_3 pebbles met target values of the above-described properties, and the irradiation test using these pebbles have been carried out in the JMTR.

4. Conclusion

The results of fabrication tests and characterization of the two kinds of Li_2TiO_3 pebbles are summarized as follows. The Li_2TiO_3/PVA/H_2O contents of 40/4.5/55.5 wt% and the nozzle diameter of 2.4 mm were selected for fabrication of Li_2TiO_3 pebbles with 2 mm diameter by the wet process using the dehydration reaction. On the other hand, the contents of sodium alginate/4HF/H_2O in the solution were selected as 1/20/79 wt%, and the content of Li_2TiO_3 powder was selected as 5 wt% for fabrication of Li_2TiO_3 pebbles with 0.3 mm diameter by the wet process using the substitution reaction. The density of Li_2TiO_3 pebbles fabricated by both

Table 1
Characterization of two kinds of Li_2TiO_3 pebbles fabricated by indirect wet processes

Items		Pebbles	
Property	Method	Large pebbles	Small pebbles
Crystalline structure	XRD analysis	Li_2TiO_3	Li_2TiO_3
Fabrication method	–	Wet process using the dehydration reaction	Wet process using the substitution reaction
Diameter	Sieve classification	1.7–2.36 mm (∼1.9 mm av.)	0.25–0.3 mm (∼0.27 mm av.)
Sphericity	Photographic analysis	1.07	1.11
Density	Liquid immersion method (Hg)	2.86 g/cm^3	2.82 g/cm^3
Grain size	SEM observation	1.9 μm	4.3 μm
Collapse load	Autograph	73.4 N	4.57 N

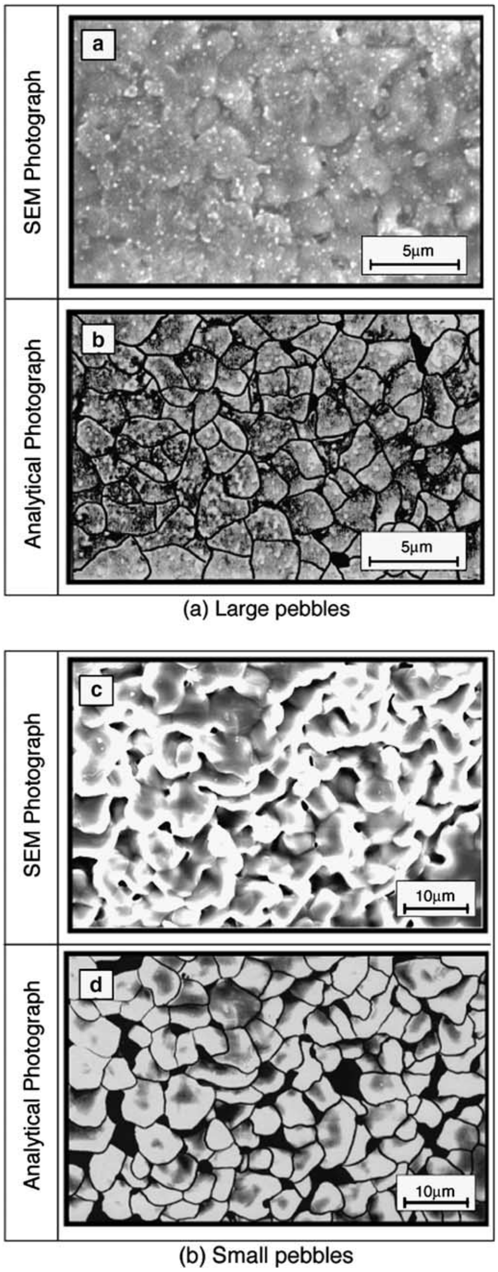

Fig. 6. SEM photographs (a,c) and analytical photographs (b,d) of large (a,b) and small (c,d) Li_2TiO_3 pebbles fabricated by indirect wet processes.

of these two kinds of wet processes was well controlled between 80% and 85% TD, and the average grain size of the Li_2TiO_3 pebbles was a satisfactory value smaller than 5 μm.

From these results of the fabrication tests and characterization, bright prospects were obtained concerning mass production of Li_2TiO_3 pebbles with a target diameter of 0.2–2.0 mm and a target density of 80–85% TD by the two kinds of indirect wet processes.

Table 2
Impurities in two kinds of Li_2TiO_3 pebbles fabricated by indirect wet processes

Elements	Content (wppm)	
	Large pebbles	Small pebbles
Ca	<2	18
Na	82	39
K	<2	2
Mg	<2	6
B	<5	<5
Si	14	73
Zr	<2	<2
Mn	<2	<2
Fe	<2	25
Co	<0.5	<0.5
Al	9	23
C	77	20
Zn	2	22

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