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Fabrication of Li_2TiO_3 pebbles by the extrusion–spheronisation–sintering process

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Abstract

Li_2TiO_3 pebbles are a ceramic breeder material option for the helium cooled pebble bed (HCPB) blanket being developed in the EU. The extrusion–spheronisation–sintering process was selected in order to produce Li_2TiO_3 pebbles fulfilling the HCPB blanket requirements, and is developed with an industrial collaboration. Adjustments of the fabrication process parameters allows the variation of the pebbles characteristics which, in turn, determine the behaviour of the pebbles and pebble beds. The feasibility of the fabrication by pre-industrial means is demonstrated at the 10 kg scale which is sufficient to cover the present needs for the tests. The advantage of this fabrication process to cover a wide range of characteristics is shown and the influence on Li_2TiO_3 pebble beds relevant properties, i.e., long-time annealing behaviour, thermal–mechanical behaviour, and tritium release performance is recalled. The overall results indicate both excellent prospects for the fabrication of Li_2TiO_3 pebbles and the attractiveness of their properties.

1. Introduction

Li_2TiO_3 pebbles are one of the options of ceramic breeder material for the helium cooled pebble bed (HCPB) blanket developed in the EU. The extrusion–spheronisation–sintering process was selected for the fabrication of the pebbles, as it proved to be the most appropriate one to obtain the goal characteristics. The satisfactory performance observed in the first functional tests of the so-fabricated pebbles [1] confirmed the promise and substantiated the validation with pre-industrial means of the steps of the lab-scale process. This work was made with the Ceramiques Techniques et Industrielles (CTI) firm. In agreement with previous studies [2], it was observed in the functional tests that the Li_2TiO_3 pebbles microstructural characteristics (open/closed porosity, grain size, specific surface area) are key parameters. Since this fabrication process easily allows varying the microstructural characteristics of the pebbles, it is very advantageous to tailor pebbles properties.

2. Pre-industrial fabrication of Li_2TiO_3 pebbles

The aim of the validation by pre-industrial means of the steps of the lab-scale process was to adapt the parameters at each step of the process to the pre-industrial conditions so as to reproduce lab-scale pebbles characteristics [3]. Simultaneously, strong consideration was given to simplicity, economics, and to production yield of the process.

2.1. Preparation of the Li_2TiO_3 powder

Precursors are commercial TiO_2 powder (purity > 99.5%, specific surface area 50 m^2/g) and Li_2CO_3 powder (purity > 99%, specific surface area 0.8 m^2/g). The powders are sieved in order to ensure a good de-agglomeration which is required to obtain a homogeneous mixing. Since an increase in metallic impurities was observed in the first batch of Li_2TiO_3 powder prepared by pre-industrial means as compared to lab-scale,

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the previous stainless steel sieves were replaced by nylon ones. The sieved powders are mixed in proportions corresponding to $Li/Ti = 1.9$ in the final ceramic (instead of 2, theoretically). This composition was optimised early in order to obtain the fine microstructure of the pebbles which is aimed at (<5 μm grain size). The mixture is blended in a 30 l blender. The blend is heated at 700 °C for Li_2TiO_3 formation. Changing from the laboratory furnace to the 1 m^3 industrial one required to re-determine the temperature cycle for the Li_2TiO_3 synthesis, accounting for the allowable heating rate of the electrical furnace. A single heating step, which is typical of industrial conditions instead of two heating steps with return to room temperature in between as used in the lab process, was finalised.

2.2. Shaping of Li_2TiO_3 green pebbles

This part of the process comprises several operations and makes use of specific devices. The change to pre-industrial conditions required several iterations, needed to redesign some of the lab-scale devices, and to adjust operating conditions:

- revision of the first formulation of the extrusion paste: nature, and proportion of Li_2TiO_3 powder/binder/plasticiser;
- revisit of the design of the extruding machine: availability of continuous operation, reduction of the dead volume. A multi-hole nozzle made of alumina instead of steel in order to limit metallic impurities was manufactured;
- automatisation of the cutting of the granules;
- the original spheronisation plate was coated with an organic material to avoid the contamination of the Li_2TiO_3 material by the steel elements.

2.3. Sintering of the Li_2TiO_3 green pebbles

The sintering temperature is a key parameter to adjust the microstructural characteristics of the pebbles, i.e., grain size, density, specific surface area. The objective is to obtain high density (≈90% of the theoretical density) pebbles with small grain size (1–2 μm). Such characteristics proved so far to offer a good compromise of the pebbles requisite properties in the functional tests of pebbles and pebble beds. For the sintering step, use was made of the same electrical furnace and of the same boats as for the preparation of the Li_2TiO_3 powder, thereby saving the equipment costs. The typical impurity analysis of the Li_2TiO_3 pebbles is given in Table 1. The main characteristics of the Li_2TiO_3 pebbles as a function of the sintering temperature are listed in Table 2. Advantage is taken of adjusting the sintering temperature to tailor the pebbles properties and the pebble beds behaviour. Examples are given in Section 3 showing the effect of the sintering temperature on important properties such as the high-temperature long term annealing behaviour, thermal creep of pebble beds, and tritium release behaviour.

At this stage of the development of the extrusion process for the fabrication of 1 mm Li_2TiO_3 pebbles in the 5–10 kg range, it was demonstrated that:

- the process allows to obtain pebbles with high purity and fulfilment of the goal characteristics;
- the process is relatively simple and inexpensive;
- the process is flexible and can be adjusted to a range of pebbles specifications (pebble size, pebble density, pebble grain size).

Table 1
Typical impurity analysis of Li_2TiO_3 pebbles

Major impurities	Content (ppm)
Al	5
Ca	20
Cr	1.5
Fe	7
K	8
Ni	3
S	1
Si	30
Na	30
C	50
Other elements	<10

Table 2
Characteristics of the sintered pebbles

Sintering temperature (°C)	Pebble size (mm)	Porosity (%)		Bed density (g/cm³)	Grain size (μm)	Average crush load (*N*)
		Open	Closed			
950	0.8–1.2	13	4	1.71	0.5–1	52
1050	0.8–1.2	5	5	1.80	1–2	66
1100	0.8–1.2	6	5	1.81	1.5–5	40
1140	0.8–1.2	5	5	1.86	2–7	38

The current fabrication facility at CTI allows the production of 150 kg/year of Li_2TiO_3 pebbles.

3. The extrusion–spheronisation–sintering process to tailor properties of Li_2TiO_3 pebbles and behaviour of pebble beds

Variation of the microstructural characteristics of the Li_2TiO_3 pebbles enabled us to identify the characteristics leading to pebbles best performance. The best performance so far was found for pebbles sintered at 1050 °C which were chosen as the current reference. Results of the main functional tests performed with Li_2TiO_3 pebbles sintered at 950, 1050, 1100 and 1140 °C are reported below.

3.1. High-temperature long term behaviour

The Li_2TiO_3 pebbles behaviour on high-temperature long-term annealing is investigated both at CEA in static air and at FZK in a $He + 0.1\%H_2$ stream at 970 °C during 3 months. The latter conditions simulate those at DEMO end-of-life at the higher operating temperature of the HCPB breeder. Effects observed to-date either in air or in $He + 0.1\%H_2$ stream are quite comparable except for the colour of the ceramic which remains white in the air atmosphere but turns black in $He + 0.1\%H_2$. Annealing test results for Li_2TiO_3 pebbles sintered at 1050 °C were reported in [4,5]. During the long-term annealing at 970 °C fine-grained reference Li_2TiO_3 pebbles undergo some significant grain growth. There is a little increase in density, too. However, no significant change in crush load values can be observed after the test. Results obtained on annealing at 970 °C in air at CEA specimens of Li_2TiO_3 pebbles sintered at 950 and 1050 °C are summarised in Table 3. According to expectations, changes (weight loss and grain growth) are larger for the pebbles sintered at lower temperature.

3.2. Uniaxial compression tests and creep tests of Li_2TiO_3 pebble beds

Uniaxial compression tests and creep tests of Li_2TiO_3 pebble beds were made at FZK between room temperature and 850 °C and 3–6.5 MPa [6]. Thermal creep tests of beds of Li_2TiO_3 pebbles sintered at different temperatures show that thermal creep strain increases with decreasing sintering temperature of the pebbles. Fig. 1 displays the thermal creep curves for the Li_2TiO_3 pebbles sintered at different temperatures at a pressure of 6.6 MPa, and at 750 °C. From the present results it is difficult to draw final conclusions with respect to the development of a thermomechanically optimised titanate pebble bed. If strong bed deformations are unfavourable, then high

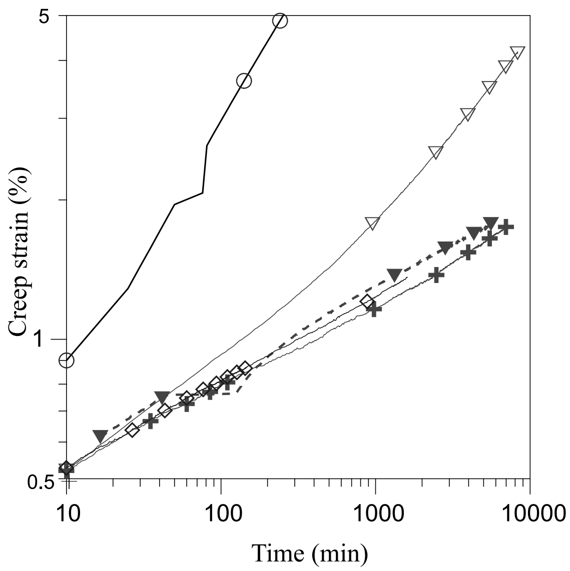

Fig. 1. Thermal creep for beds of Li_2TiO_3 pebbles sintered at 950 °C (○), 1050 °C (▽), 1100 °C (◇) and 1140 °C (+) at a pressure of 6.6 MPa and at 750 °C.

Table 3
Behaviour of Li_2TiO_3 pebbles annealed at 970 °C in air

Sintering temperature (°C)	Property	As-sintered	970 °C (1 month)	970 °C (2 months)	970 °C (3 months)
950	Weight loss (%)	–	0.04	0.06	0.08
	Open porosity (%)	13	–	–	–
	Closed porosity (%)	4	–	–	4
	Crush load (*N*)	52	58	48	52
	Grain size (μm)	0.5–1	4–14	5–19	6–22
1050	Weight loss (%)	–	0.01	0.03	0.04
	Open porosity (%)	5	–	–	4
	Closed porosity (%)	5	–	–	3
	Crush load (*N*)	66	61	61	63
	Grain size (μm)	1–2	3–11	4–13	3–20

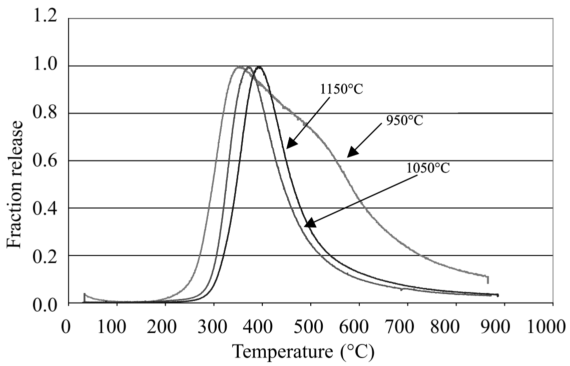

Fig. 2. Comparative out-of-pile tritium release tests of Li_2TiO_3 pebbles sintered at 950, 1050 and 1150 °C.

sintering temperatures and high density should be chosen. However, larger creep strains, corresponding to lower sintering temperatures, might accommodate irradiation-induced swelling. Irradiation experiments are planned to investigate the swelling issue.

3.3. Tritium release behaviour

Out-of-pile tritium release tests are very useful to evaluate/rank the behaviour of ceramic breeder pebble fabricated under various conditions. Comparative out-of-pile tritium release tests of Li_2TiO_3 pebbles sintered at CEA at 950 and 1150 °C, and of the reference 'semi-industrial' Li_2TiO_3 pebbles sintered at 1050 °C were made at NRG [7]. Results displayed in Fig. 2 show that the curves rank in the same order as the sintering temperatures of the Li_2TiO_3 pebbles. The curve for the semi-industrial Li_2TiO_3 pebbles shows a narrow peak at 370 °C, along with a return to the background noise faster than observed for the other specimens, indicating a better behaviour of the semi-industrial reference pebbles. In accordance with expectations, it appears that the temperature of the release peak is lower for pebbles with smaller grain size and with lower density. Eventhough tritium release is not as good at higher densities than at lower ones, it remains quite satisfactory. Therefore, high densities along with sufficiently small grain sizes should be aimed at, since the tritium release behaviour may not be significantly degraded, while other properties such as thermal conductivity and mechanical strength are expected to be improved.

4. Conclusion

The extrusion–spheronisation–sintering process was finalised at the semi-industrial scale for the production of the very pure, 1 mm Li_2TiO_3 pebbles fulfilling the HCPB blanket requirements. The current facility at CTI allows the production of 150 kg/year of Li_2TiO_3 pebbles which is sufficient for the present needs. The process can be easily extrapolated to industrial scale as it makes use of conventional techniques of the ceramic industry. Owing to its great flexibility, the process is very suitable to tailor the pebbles properties and the pebble beds behaviour, as the functional tests have shown which are in progress in the European blanket program. Exploring the whole range of pebbles diameters achievable by the extrusion process is currently under study, especially exploring the lower diameter limit since smaller pebbles are likely to ease the blanket filling procedure, and increase pebble bed density and thermal conductivity. In addition, in view of the necessary utilisation in the future of costly ^6Li enriched ceramic pebbles, focus is being placed on the minimisation of production losses as well as on the recycling process of the unburnt ^6Li in the Li_2TiO_3 pebbles after service in a reactor.

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