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Properties of lithium metatitanate pebbles produced by a wet process

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Abstract

Lithium metatitanate (Li_2TiO_3) is considered as one of the candidate materials for the ceramic breeder in both the ITER Breeding Blanket and the European Helium Cooled Pebble-Bed Blanket for DEMO. A wet process based on powder-gelation for the manufacture of Li_2TiO_3-pebbles is described. Pebble characteristics and its basic properties are given along with results of out-of-pile tritium release experiments.

1. Introduction

Lithium metatitanate (Li_2TiO_3) is considered as a candidate material for the ceramic breeder in both the Helium Cooled Pebble-Bed Blanket for DEMO and the ITER Breeding Blanket along with lithium orthosilicate (Li_4SiO_4) and metazirconate (Li_2ZrO_3). The Li_2ZrO_3 shows a better tritium release behaviour at low temperatures as compared to the Li_4SiO_4, which has been demonstrated in a number of irradiation experiments, like EXOTIC-5 to -7 [1–4]. Lithium titanate is expected to behave similarly to the metazirconate, but will have the additional advantage of a much lower activation [4,5]. The manufacturing of ceramic pebbles by sol–gel method is considered as a possible economically attractive route, and it will enable reprocessing lithium from the breeding blanket waste [6].

In a pre-study of ECN on fabrication of breeder materials, it was demonstrated that a wet process based on powder gelation is a viable option to produce lithium titanate as spherical pebbles with promising characteristics. The target for the development work for the pebble-bed blankets was then set to obtain pebbles with diameter in the range 0.5–1 mm, and having at least 80% of theoretical density. At first the objective of the work at ECN has been to optimize the production process for Li_2TiO_3 pebbles on a laboratory scale. The production on the laboratory scale should provide appropriate quantities of Li_2TiO_3 pebbles for characterization and the performance of irradiation experiments, e.g. in EXOTIC-8 [7]. The paper describes the production technique applied and the major pebble characteristics.

This work has been performed in 1996 as a part of the European Blanket Project (EBP), as a subtask within the Helium Cooled Pebble-Bed Blanket-subproject.

2. Pebble development

The basic idea of the lithium titanate pebble development at ECN has been to produce the pebbles via a wet process involving gelation of powders of lithium carbonate Li_2CO_3 and titanium dioxide TiO_2 and to obtain lithium titanate by the solid state reaction:

$$Li_2CO_3(s) + TiO_2(s) \rightarrow Li_2TiO_3(s) + CO_2(g) \uparrow .$$

For the very first trial mixtures polyvinylalcohol (PVA) has been used as a binder and the slurry was injected through a nozzle into a cold toluene bath. The pebble shape appeared to be very sensitive to experimental variations and was difficult to reproduce. It has also been tried to accelerate the droplet detachment from the nozzle opening by several means like flowing air, mechanical vibration, varying nozzle geometry as well as by change of the slurry characteristics. Gradually the following consistent recipe has been developed based on an organic solution in water as the binder material.

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2.1. Production route for Li_2TiO_3 pebbles

Within the scope of the present work, it was decided to use commercial powders for the production of Li_2TiO_3 pebbles. The lithium carbonate (Li_2CO_3) is 99.9% pure CERAC powder. It is pulverized and sieved into the fraction <0.053 mm. The titanium dioxide (TiO_2) powder is Degussa P25 with purity >99.5% and grain size 15–40 nm (aerosol quality). The powders are weighed in the desired stoichiometric ratio and mixed with a solution of hydroxy-ethyl-cellulose (3% Natrosol). The solid amounts to about 20% of the slurry. The slurry has some foamy appearance due to air inclusions originating from the addition of the fine powders, which has therefore to be evacuated carefully. From this slurry droplets are injected (by gravity) in a 220 K toluene bath. A stainless steel nozzle was applied with inner/outer diameter of 0.25/0.45 mm. The viscosity of the slurry has been modified by a silicon-based anti-foaming agent to decrease the droplet size. The gel-spheres are frozen rapidly and slowly sink to the bottom. Freeze drying is performed batchwise for some days at 270 K.

The calcination step is performed in open Y_2O_3 crucibles in a Retsch furnace for 4 h at 875 K, with a ramp rate of 60 K/h in a dry oxygen atmosphere. Sintering has been performed by subsequent heating at a rate of 100 K/h up to 1450–1475 K and holding this temperature for 12 h.

2.2. Pebble characteristics

A quantity of 40 g of Li_2TiO_3 pebbles has been produced according to the process described above. The pebbles were typically sized in the range 0.3–1.2 mm. A sieved fraction of 0.5–1.0 mm sized pebbles is considered as the usable end-product. The pebbles are typically only slightly ellipsoidal, with occasional appearance of cracks from sintering. Values for pebble density were derived both from dimensional measurements and by mercury porosimetry (Quantachrome Autoscan-33). Packing

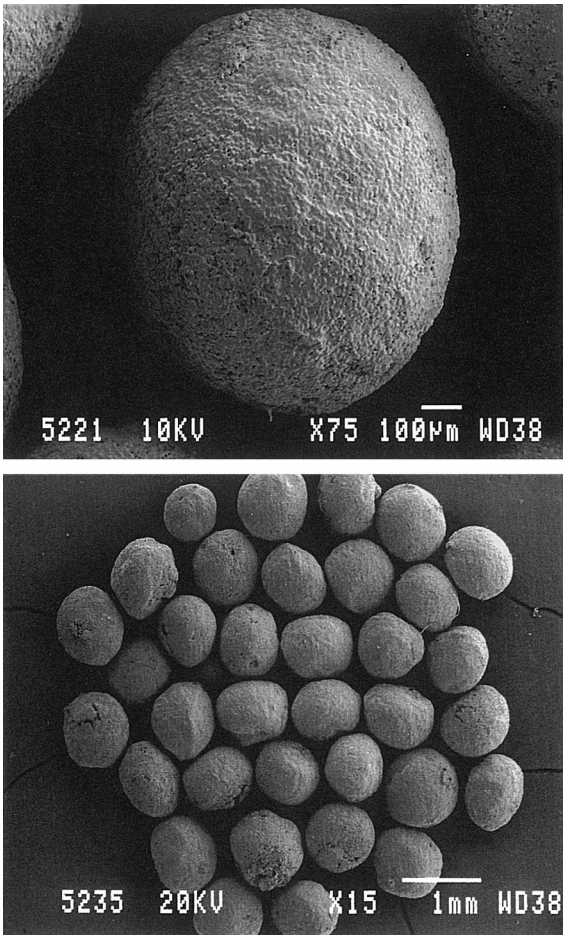

Fig. 1. SEM micrographs of Li_2TiO_3 pebbles produced at ECN by the wet process.

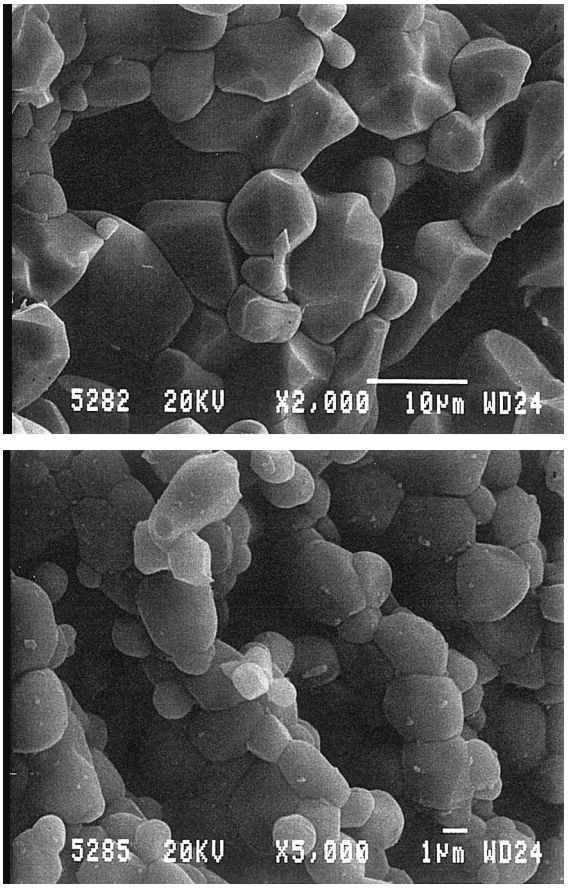

Fig. 2. Li_2TiO_3 pebbles produced at ECN by the wet process: (a) fracture surface appearance and (b) details of (a).

Table 1
Characteristics of Li_2TiO_3 pebbles produced at ECN

Parameter	Value	Units	Fraction
Li_2TiO_3 theoretical density [8]	3.43	g/cm^3	100% T.D
Pebble density derived from main diameter	2.55	g/cm^3	74.3% T.D
Pebble density by mercury porosimetry	2.71	g/cm^3	79% T.D.
Open pore volume			18.9% T.D.
Closed pore volume			2.1% T.D.
Smear density of 10 cm^3 pebbles	1.63	g/cm^3	48% T.D.
Effective packing density (10 cm^3)	60	%	
Grain size	5–10	μm	

density of a pebble bed was derived for a 10 cm^3 cylindrical volume. The pebble characteristics are given in Table 1.

According to X-ray diffraction measurements the pebbles are monoclinic Li_2TiO_3. Fig. 1 shows the typical results from scanning electron microscopy. Fig. 2 shows the details of pebble fracture surfaces. The grain size of the pebbles was found to be typically 5–10 μm.

3. Tritium doping and annealing experiments

3.1. Experiments and results

A short duration radio-isotope irradiation ('tritium doping') has been performed on small quantities of Li_2TiO_3 pebbles along with some Li_2TiO_3-pellet material from CEA [5]. This material has about 82% of the theoretical density and a grain size of about 1 μm. Fig. 3 shows its fracture surface appearance.

The materials were placed in two closed quartz capsules within a sealed aluminium container and irradiated for 1 h in the HFR RODEO facility. The amounts of produced tritium were 3–4 mCi/g of which about half was found resident in the specimens.

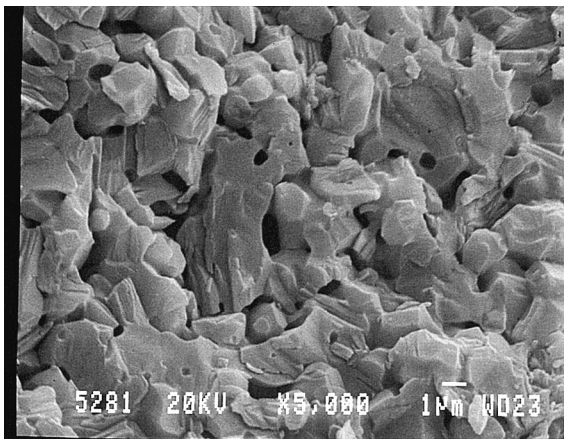

Fig. 3. Typical fracture surface of CEA Li_2TiO_3 pellet material.

Temperature Programmed Desorption (TPD) experiments have been performed at heating rates of 1, 2.5, 5 and 10 K/min up to a maximum of 850°C in the reference purge gas He+0.1% H_2, similar to earlier cases [1]. The results obtained for the ECN pebbles are shown in Fig. 4. Analysis of the TPD curves shows two major release peaks at temperatures around 200°C and 400°C (for 1 K/min heating rate). The apparent increase in the release rate near 800°C is a system effect, for which no corrections were made. The residual tritium after the test has been measured by dissolution method and liquid scintillation counting and was found negligible. The release peak at the higher temperature (400°C) clearly dominates the preceding one (at 200°C). This behaviour is in contrast to results obtained for the CEA pellets: for this material, the release peak at the lower temperature was found far more dominant. For comparison, one of the curves obtained for the CEA pellet material is also shown in Fig. 4.

Fig. 5 shows some results of isothermal annealing for the same materials at temperatures in the range 250–400°C. Also here the CEA material shows higher release rates as compared to the ECN pebbles.

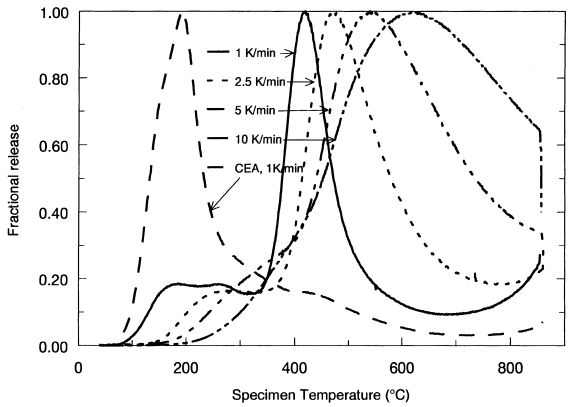

Fig. 4. Out-of-pile release from 'tritium doped' ECN Li_2TiO_3 pebbles by temperature programmed desorption at heating rates of 1, 2.5, 5 and 10 K/min. Results obtained on CEA Li_2TiO_3 pellets for 1 K/min are added for comparison.

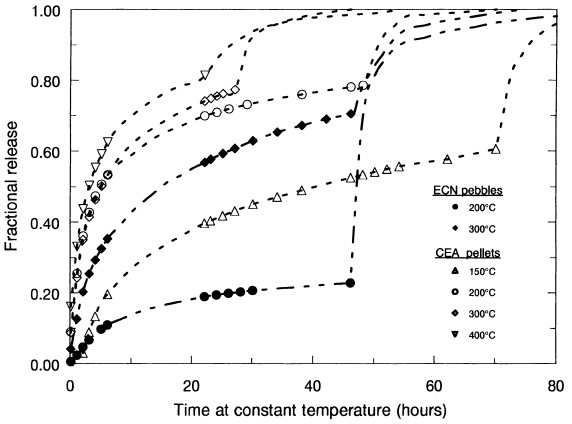

Fig. 5. Tritium release of Li_2TiO_3 pellets (CEA) and pebbles (ECN) on isothermal annealing for various temperatures.

3.2. Discussion

A major difference between the two types of material is the grain size (1 vs. 5–10 μm), while values for open and closed porosity are comparable. Furthermore, the ECN pebbles are stoichiometric while CEA pellets are under stoichiometric (by 5% in lithium). It has to be noted that in out-of-pile annealing tests on lithium titanates at the CEA laboratory, including the same pellet material, only one release peak was observed [9]. In those observations, the peak was located at about 335°C at a heating rate of 1 K/min, i.e. between the presently reported values of ~190°C (CEA pellet) and ~420°C (ECN pebbles), see Fig. 4.

The temperature values wherein the tritium release shows a (local) maximum were used to derive activation energies [1]. Due to the system effects and poor statistics only indicative values can be given:

- Peak I: E_a ~25–30 kJ/mol,
- Peak II: E_a ~55–60 kJ/mol.

The physico-chemical mechanisms responsible for the observed behaviour of the two lithium titanates will have to be identified in order to optimize this newly developed class of materials for application in a breeding blanket. Further experiments are planned for verifications, while first in-pile test results for these materials are expected in 1998 [7].

4. Conclusions

- It has been shown that lithium titanate (Li_2TiO_3) pebbles can be manufactured by a wet process based on powder gelation, with promising characteristics in view of use in a tritium breeding blanket.
- Further development efforts for the lithium titanate pebbles will have to be devoted to scaling-up of the manufacturing process and improvement of pebble-characteristics, in particular towards increasing pebble density and the packing factor of the pebble-bed.
- Out-of-pile annealing experiments have been performed on 'tritium doped' pebbles along with some pellet material from CEA. Results of temperature programmed tritium desorption reveal the presence of at least two peaks. Materials showed distinct differences, which was also observed in isothermal annealing experiments.
- The tritium release behaviour of Li_2TiO_3, of which first results show distinct differences for ECN pebbles and CEA pellet material, needs further out-of-pile studies along with in-pile test results to determine optimization steps for this newly developed class of breeder materials.

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