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Section 12. Blanket materials and engineering

Behaviour of Li_2ZrO_3 and Li_2TiO_3 pebbles relevant to their utilization as ceramic breeder for the HCPB blanket

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Abstract

Li_2ZrO_3 and Li_2TiO_3 pebbles are being investigated at Commissariat à l'Energie Atomique as candidate alternative ceramics for the European helium-cooled pebble bed (HCPB) blanket. The pebbles are fabricated using the extrusion–spheronization–sintering process and are optimized regarding composition, geometrical characteristics, microstructural characteristics, and material purity. Tests were designed and are being performed with other organizations so as to check the functional performance of the pebbles and pebble beds with respect to the HCPB blanket requirements, and, finally, to make the selection of the most appropriate ceramic for the HCPB blanket. Tests include high temperature long-term annealing, thermal shock, thermal cycling, thermal mechanical behaviour of pebble beds, thermal conductivity of pebble beds, and tritium extraction. Current results indicate the attractiveness of these ceramics pebbles for the HCPB blanket. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Li_2ZrO_3 and Li_2TiO_3 pebbles are being investigated at Commissariat à l'Energie Atomique as alternative ceramic breeder material for the helium-cooled pebble bed (HCPB) blanket developed within the European blanket project. The selection of one ceramic between the reference (Li_4SiO_4) and the alternative is an important objective of the HCPB blanket program. Since such a selection can be made only with equivalent properties databases for the three candidates, the determination of the relevant properties of pebbles and of the behaviour of pebble beds are major issues being addressed in the experimental program together with the finalization of the fabrication processes of the pebbles. The study of Li_2ZrO_3 and Li_2TiO_3 pebbles is summarized.

2. Characterization and optimization of Li_2ZrO_3 and Li_2TiO_3 pebbles

A preliminary set of specifications for the pebbles was fixed at Commissariat à l'Energie Atomique: (a) spherical shape, (b) pebble size around 1 mm with a narrow size distribution, (c) highest possible pebble density, provided tritium release is not unduly affected, (d) small grain size, which favours both tritium release and mechanical strength, and (e) high purity of the final product.

Following the evaluation of the two fabrication processes, i.e., the agglomeration–sintering process and the extrusion–spheronization–sintering process, the latter was selected in 1998 for further development. The process has the advantage of being applicable to the fabrication of both Li_2ZrO_3 and Li_2TiO_3 pebbles. Pebbles have nearly a spherical shape, a narrow size distribution, and their density can be tailored by adjusting the fabrication process parameters. In addition, the process makes use of conventional techniques of powder technology and, therefore, industrial production is not expected to raise any significant problem. In order to address the scalability of fabrication to large quantities, pebbles shaping, which is a major step in the process,

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was accomplished through the collaboration and the facilities of an industrial firm.

The steps of the fabrication process include:

- Preparation of the Li_2ZrO_3 and Li_2TiO_3 powders using the solid-state reaction of Li_2CO_3 powder, and ZrO_2 (Hf < 50 ppm) and TiO_2 powders. Proportions are chosen so as to obtain the compositions 0.95 Li_2ZrO_3, 0.05 ZrO_2, and 0.95 Li_2TiO_3, 0.05 TiO_2 which were optimized to obtain a small grain size material.
- Preparation of the paste and extrusion.
- Cutting of granules.
- Spheronization of granules.
- Sintering.

A parametric study allowed the identification of suitable conditions to meet the fixed specifications. Pebble shape was improved during the successive trials and can be considered now to be as spherical as practicable when starting from cylindrical granules. Size distribution, 0.9–1.2 mm, is satisfactory. For Li_2ZrO_3 pebbles, a density of ~86% T.D. (determined from open porosity) and a grain size of ~1 μm were typically obtained. For Li_2TiO_3 pebbles, a density of ~93% T.D. (determined from open porosity) and a grain size of 1–2 μm were typically obtained. For both the ceramics, the impurity analysis (as evaluated by Spark source mass spectrometry) indicates that there are few elemental impurities and that the amount (<50 ppm) is sufficiently low [1].

Once goal geometrical, microstructural, and purity characteristics were reached, the subsequent stage was to verify the suitable performance of the pebbles as regards the HCPB blanket requirements. Otherwise, further adjustment of the fabrication parameters would be needed in order to tailor pebbles properties.

According to the results of the testing campaign (see Section 3), the current characteristics of the Li_2ZrO_3 pebbles are found quite satisfactory to meet the HCPB requirements, and are therefore retained. The current characteristics of the Li_2TiO_3 pebbles are found adequate too. However, in view of the better tritium release behaviour observed in the EXOTIC-8 experiment of Li_2TiO_3 pebbles and pellets, both with a density lower than 90% T.D., a slightly lower density is aimed at, provided such a density change does not induce an unacceptable degradation of any other key properties.

3. Performance evaluation of Li_2ZrO_3 and Li_2TiO_3 pebbles and pebble beds

During blanket operation, the ceramic breeder pebbles and pebble beds will be subjected to several effects which could be detrimental to safe operation. These effects need to be quantified for proper blanket design analysis, and hence, for ensuring satisfactory blanket performance. To this end, out-of-pile tests and in-pile tests were designed which simulate the HCPB blanket operating conditions regarding temperature, temperature gradients, pressure, mechanical stress, lithium burn-up etc. Performance evaluation tests performed to-date include:

3.1. High temperature, long-term annealing tests

The tests aim at checking the maximum allowable temperature of the ceramic. Tests are made at Commissariat à l'Energie Atomique, in air at 900°C, 1000°C, and 1200°C for up to 3 months, as well as at Forschungszentrum Karlsruhe, in $He + 0.1\%$ H_2 (the reference purge gas of HCPB) at 970°C for 96 days [2]. The latter conditions are estimated to simulate those of the breeder (Li_4SiO_4) maximum nominal temperature (~900°C) in the HCPB blanket during DEMO lifetime (20 000 h). The relationship between the annealing temperature and the maximum nominal temperature in the HCPB blanket has been determined on the basis of the creep activation energy, because for Li_4SiO_4 (reference ceramic) creep is the most important phenomenon at the maximum nominal temperature. According to expectations, the higher the annealing temperatures larger are the changes on annealing. However, no significant changes could be observed for the Li_2ZrO_3 pebbles on annealing at ~1000°C in air or at 970°C in $He + 0.1\%H_2$, but moderate grain growth and little lithium vaporization. A large grain growth was observed for the Li_2TiO_3 pebbles, but the crush load value for single pebbles remained almost stable. No lithium vaporization could be detected. The Li_2TiO_3 pebbles turned black on annealing in $He + 0.1\%$ H_2. The colour, which disappears on heating in air, is assigned to oxygen substoichiometry and does not seem to affect pebble properties.

3.2. Uniaxial compression tests

Uniaxial compression tests of Li_2ZrO_3 and Li_2TiO_3 pebble beds were performed by Forschungszentrum Karlsruhe in order to determine the stress/strain relationships as well as thermal creep strains at constant pressure. The experiments were performed between ambient temperature and 850°C and at pressures up to 6.5 MPa. Three different kinds of Li_2TiO_3 materials were tested, differing in the sintering temperature which governs the microstructure: 1100°C, 1050°C and 950°C, as well as in pebble size: 1.1–1.5 and 0.9–1.2 mm.

For Li_2ZrO_3, the pressure dependence on strain is smaller than for Li_2TiO_3 and is comparable to that of Li_4SiO_4 [3]. For a temperature range between ambient and about 600°C, this dependence is fairly temperature independent for all materials. At higher temperatures, the materials become increasingly softer with increasing temperature, i.e., for a given stress the strains become larger during the first pressure increase and thermal creep increases as well. Fig. 1 shows this temperature dependence for titanate sintered at 1050°C. For titanate sintered at 950°C, the temperature dependence is even more marked.

The sintering temperature also influences thermal creep, see Fig. 2. Thermal creep increases with decreasing sintering temperature. The figure shows that the results for Li_2ZrO_3 are similar to that of Li_2TiO_3 sintered at 1100°C. Thermal creep of Li_4SiO_4 pebble beds [4] is between that of Li_2TiO_3 sintered at 1050°C and Li_2TiO_3 sintered at 1100°C.

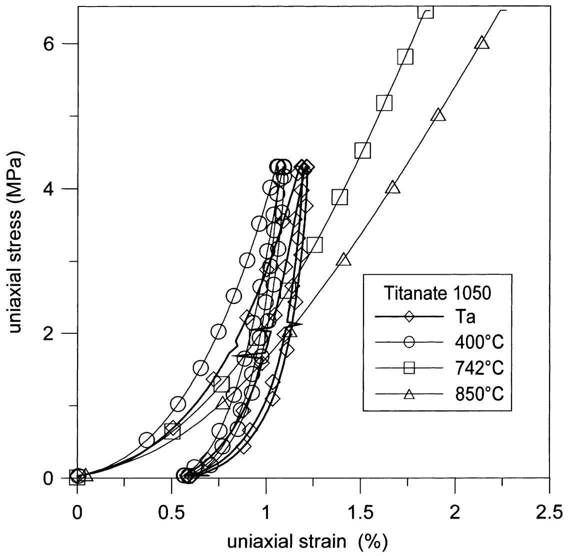

Fig. 1. Uniaxial stress versus uniaxial strain for a bed of Li_2TiO_3 pebbles sintered at 1050°C. First pressure increase and two cycles at ambient temperature and 402°C, first pressure increase at 742°C and 850°C.

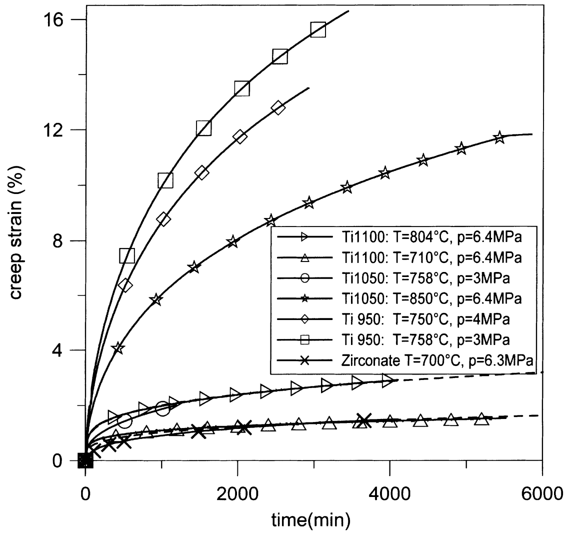

Fig. 2. Thermal creep for beds of Li_2TiO_3 pebbles sintered at 950°C (Ti 950), 1050°C (Ti 1050), 1100°C (Ti 1100), and of Li_2ZrO_3 pebbles sintered at 1100°C.

Post-examination of the 700°C test specimen showed that the Li_2ZrO_3 pebbles were negligibly agglomerated; the Li_2TiO_3 pebbles sintered at 1100°C were somewhat more agglomerated, however, these pebbles could still be separated by very small mechanical forces. Again, this agglomeration increases both with operational temperature and with decreasing sintering temperature.

3.3. Thermal conductivity test

Thermal conductivity tests of the pebble beds was measured using the hot-wire method at Japan Atomic Energy Research Institute, Naka as part of the International Energy Agency collaboration activity and are reported in [5].

3.4. Thermal cycling tests

The thermal cycling performance of pebble beds was studied at Commissariat à l'Energie Atomique at 15°C/s during 300 cycles in the range 170–600°C, and 350–800°C. No change in microstructure, nor fragmentation of the pebbles was observed under these conditions for any of the two ceramics. No change in crush load for Li_2TiO_3 pebbles but a slight decrease for Li_2ZrO_3 pebbles were observed. Two types of thermal cycling tests of Li_2TiO_3 pebbles were performed at Forschungszentrum Karlsruhe. The objective of the first type of test earlier described in [6] was to determine the resistance of the pebbles to thermal shocks. Therefore, very fast temperature transients were applied to the pebble bed. In this case, no attempt was made to obtain the maximum packing factor of the pebble bed (the container was filled without vibration operation) to avoid the stresses caused by the relative dimensional variations between pebble bed and container during the temperature transients. The thermal shock test of Li_2TiO_3 pebbles was made during 500 cycles between 250°C and 600°C, at a cooling rate up to ~70°C/s, in He atmosphere. A few pebbles were broken during the test and some turned brown. There was no change in microstructure, but a slight decrease in crush load, which returned to its initial value after heat treatment of the pebbles in air. The second type of thermal cycling [6] aimed at studying the effects of the stresses caused by the different thermal expansion between the pebble bed and the container walls. Thus, the tests were performed with Li_2TiO_3 pebble beds with a maximum packing factor. This was obtained by thoroughly vibrating the pebble bed. This test was made during 500 cycles between 350°C and 600°C with He flowing through the pebble bed. A cooling rate of 5°C/s was obtained after the heating phase in an oven by cooling the pebble bed container with uniformly distributed air jets. A negligible amount of pebbles were broken during the test. No cracks were observed on the pebbles after the test. There was no change in microstructure but a slight decrease in crush load, which returns to its initial value after heat treatment of the pebbles in air. Thermal shock and thermal cycling tests were performed under the same conditions for Li_2ZrO_3 pebbles. In this case too, a negligible amount of pebbles were broken. Pebbles turned brown after the thermal shock test and light beige after the thermal cycling test.

3.5. Irradiation tests

Irradiation performance was studied in the EXOTIC-8 experiments designed and performed in the high flux reactor at Petten by Nuclear Research Group in collaboration with Joint Research Centre, Petten. Both in situ tritium release experiments with Li_2ZrO_3 and Li_2TiO_3 pebbles, and a high burn-up test with Li_2TiO_3 pebbles were/are performed. In the in situ tritium release experiment, differential tritium inventories following temperature transients are measured, allowing to calculate tritium residence times. The high burn-up test of Li_2TiO_3 pebbles is running a lithium burn-up of ~15% and is expected to be reached at the end of the test. Detailed results are reported in a companion paper [7]. Tritium residence times are plotted in Fig. 3 as a function of reciprocal temperature. Results confirm the excellent tritium release behaviour of the Li_2ZrO_3 pebbles (identification EXOTIC-8/# 6) which was already observed in a number of experiments worldwide. Results for the Li_2TiO_3 pebbles are not as good, eventhough adequate for the HCPB blanket. The better results obtained for both Li_2TiO_3 pebbles (identification-8/# 1) produced by an agglomeration process, and for Li_2TiO_3 pellets (identification EXOTIC-8/# 2) which have a lower density than Li_2TiO_3 pebbles (identification EXOTIC-8/# 5) suggest some margin for improvement. The higher tritium residence times observed for the Li_2TiO_3 pebbles (identification EXOTIC-8/# 5) are likely due to the relatively high fraction of closed porosity.

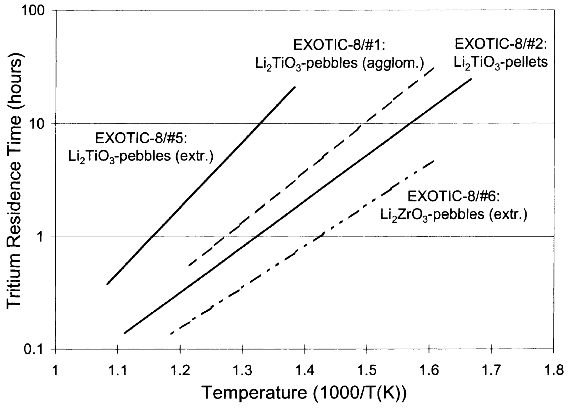

Fig. 3. Tritium residence times versus temperature, obtained in the EXOTIC-8 in-pile experiments for Li_2ZrO_3 pebbles, Li_2TiO_3 pebbles and Li_2TiO_3 pellets (extr.: extrusion process; agglom.: agglomeration process).

4. Conclusion

The extrusion–spheronization–sintering process was worked out at lab-scale for the fabrication of low impurity content, ~1 mm diameter Li_2ZrO_3 and Li_2TiO_3 pebbles, with high density and small grain size, capable to fulfill the HCPB blanket requirements. Scaling-up the production to kg-quantities is underway [8]. The high temperature annealing behaviour under conditions simulating both the maximum breeder temperature and the lifetime of the DEMO blanket is found acceptable. Current results of the thermal–mechanical behaviour of HCPB typical pebble beds are satisfactory. Results of the tritium release behaviour of the Li_2ZrO_3 pebbles are excellent. The tritium release behaviour of the Li_2TiO_3 pebbles is adequate nevertheless some improvement is being searched. Thermal conductivity measurements of pebble beds are available. Thermal shock and thermal cycling behaviours are satisfactory. The irradiation behaviour of Li_2TiO_3 pebbles is being investigated while that of Li_2ZrO_3 pebbles is, since long, known to be very good.

In brief, current performance evaluation results are good and affirm the attractiveness of both Li_2ZrO_3 and Li_2TiO_3 ceramic pebbles for utilization in the HCPB blanket.

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