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Li_4SiO_4 based breeder ceramics with Li_2TiO_3, $LiAlO_2$ and $Li_XLa_YTiO_3$ additions, part II: Pebble properties

M.H.H. Kolb[a,*], R. Knitter[a], T. Hoshino[b]

[a] Karlsruhe Institute of Technology, Institute for Applied Materials, PO Box 3640, 76021, Karlsruhe, Germany
[b] Breeding Functional Materials Development Group, Department of Blanket Systems Research, Rokkasho Fusion Institute, Fusion Energy Research and Development Directorate, National Institutes for Quantum and Radiological Science and Technology (QST), Japan

HIGHLIGHTS

- The mechanical strength of Li_4SiO_4-based breeder pebbles can be improved by adding either LMT, LAO or LLTO as second phase.
- The increase in strength is closely linked to a reduction of the open porosity of the pebbles.
- All fabricated pebbles show a highly homogenous microstructure with mostly low closed porosity.
- Adding LLTO, although it decomposes during sintering, greatly improves the strength of the pebbles.

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ABSTRACT

The pebble properties of novel two-phase Li_4SiO_4 pebbles of 1 mm diameter with additions of Li_2TiO_3, $LiAlO_2$ or $Li_xLa_yTiO_3$ are evaluated in this work as a function of the second phase concentration and the microstructure of the pebbles. The characterization focused on the mechanical strength, microstructure and open as well as closed porosity. Therefore crush load tests, SEM analyses as well as helium pycnometry and optical image analysis were performed, respectively.

This work shows that generally additions of a second phase to Li_4SiO_4 considerably improve the mechanical strength. It also shows that the fabrication processes have to be well-controlled to achieve high mechanical strengths. When Li_2TiO_3 is added in different concentrations, the determinant for the crush load seems to be the open porosity of the pebbles. The strengthening effect of $LiAlO_2$ compared to Li_2TiO_3 is similar, while additions of $Li_xLa_yTiO_3$ increase the mechanical strength much more. Yet, Li_4SiO_4 and $Li_xLa_yTiO_3$ react with each other to a number of different phases upon sintering. In general the pebble properties of all samples are favorable for use within a fusion breeder blanket.

1. Introduction

This publication constitutes the second part of two publications on lithium orthosilicate (Li_4SiO_4) based ceramic breeder pebbles with additions of lithium metatitanate (Li_2TiO_3), lithium aluminate ($LiAlO_2$) and lithium lanthanum titanate ($Li_xLa_yTiO_3$). These second phases are added to the pebbles to enhance the Li_4SiO_4-based EU reference material with regard to a possible use in a demonstration reactor (DEMO). It is clear that the conditions within solid breeder blankets are harsh. High temperatures, the effects of neutron irradiation and thermally induced mechanical stresses are highly demanding for the ceramic material. Even though the breeder material is considered as a functional material which does not contribute to the structural performance of the blanket, it has to withstand these external forces. Otherwise the pebble beds might degrade in a way so that its changed properties impede safe operation of the blanket.

In order to increase the mechanical strength of the pebbles, Li_2TiO_3 and $LiAlO_2$ were added. $Li_xLa_yTiO_3$ was added to increase the overall lithium diffusivity which might also increase the diffusivity of hydrogen isotopes and thus facilitate the release of tritium during operation [1]. It is conjectured that tritium might diffuse along the same diffusion paths through the lattice as lithium does. However, there is currently no proof. In the first part [2] the fabrication of the pebbles was addressed as well as the effect of the additions on the activation behavior of pebbles. By using the emulsion method [3], it was possible to fabricate pebbles with these additions in a reliable and economic way. A recapitulation of the

* Corresponding author.
E-mail address: Matthias.kolb@kit.edu (M.H.H. Kolb).

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fabrication process is given in the experimental section for comprehension. However, the focus of this part is on the properties of the produced pebbles as a function of the second phase additions and the pebbles' microstructure and thereby clarifying whether such pebbles qualify as potential advanced breeder pebbles.

The pebbles are characterized with regard to their mechanical rigidity, microstructure as well as open and closed porosity. Therefore crush load tests of individual pebbles, scanning electron microscopy (SEM) investigations of cross sections as well as helium pycnometry and optical image analysis were carried out, respectively. With these results, the pebble properties can be compared to the existing advanced breeder materials and the influence of the second phase additions on the pebble quality can be assessed.

2. Experimental

This section summarizes the experimental work for characterizing the produced pebbles. As it is currently considered to be one of the most critical properties of lithium orthosilicate based pebbles, special emphasis is given to the determination of the mechanical properties of the pebbles. Also the techniques to investigate the pebble density and porosity are explained in detail.

2.1. Wet-chemical fabrication of Li_4SiO_4-based pebbles

The pebbles which are characterized in this work were fabricated by an adapted emulsion process, which is based on the fabrication of single phase Li_4SiO_4 pebbles as described by Hoshino [3]. This was necessary as the melt-based fabrication is limited with respect to the melt temperature, and thus the melt composition, that can be processed [4]. The adapted emulsion process is elaborately presented in the first publication on this work, i.e. "Li_4SiO_4 based breeder ceramics with Li_2TiO_3, $LiAlO_2$ and $Li_XLa_YTiO_3$ additions, part I: Fabrication" [2].

In summary the following pebble samples were produced (nominal compositions given):

- LOS + LMT: Nine batches of LOS(Li_4SiO_4)/LMT(Li_2TiO_3) pebbles were produced covering all binary compositions in 10 mol% steps.
- LOS + LAO: Three batches of LOS(Li_4SiO_4)/LAO($LiAlO_2$) pebbles were produced with 10 mol%, 20 mol% and 30 mol% $LiAlO_2$ in LOS.
- LOS + LLTO: Four batches of (Li_4SiO_4)/LLTO($Li_{3x}La_{2/3-x}TiO_3$) pebbles were produced with 10 mol% to 40 mol% $Li_{3x}La_{2/3-x}TiO_3$ in LOS in 10 mol% steps.

The adapted emulsion process consists of several steps. In a first step a slurry is prepared from a binder solution and the starting materials Li_2CO_3 and Li_2SiO_3 to form Li_4SiO_4 upon sintering (see equation (1)) as well as additions for the anticipated second phase. For the LOS + LMT pebbles, Li_2TiO_3 powder was used. Similarly, for the LOS + LLTO pebbles $Li_{0.392}La_{0.536}TiO_3$ powder was added, while for the LOS + LAO pebbles Li_2CO_3 and Al_2O_3 were added to form $LiAlO_2$ upon sintering (see equation (2)). A defined surplus of Li_2CO_3 is necessary to countervail the lithium losses during the process.

$$Li_2CO_3 + Li_2SiO_3 \xrightarrow{\Delta E} Li_4SiO_4 + CO_2 \quad (1)$$

$$Li_2CO_3 + Al_2O_3 \xrightarrow{\Delta E} 2LiAlO_2 + CO_2 \quad (2)$$

In the second step, the starting materials were co-milled in a ball mill with ZrO_2 balls to form an homogenous slurry. Prior to the pebble fabrication, the slurry is defoamed in an ultrasonic bath. The actual fabrication of the green pebbles is carried out by cutting a precise flow of the slurry by a cross-flow of oil. The so-generated slurry segments are then led to a cold bath where the slurry forms spherical droplets and the binder gels. After removing the gel spheres from the bath, the spheres are dried to form the green pebbles. These pebbles are then sintered at 1273 K for 5 h independent of their composition.

2.2. Crush load determination

The mechanical characterization of the breeder pebbles consists of the measurement of their ultimate compressive fracture load or crush load, as the pebbles are too small to precisely measure their strain during mechanical loading and thus to directly determine mechanical material properties in a standard way.

As the crush load is significantly dependent on the pebble size, the crush loads of the pebbles are normalized according to their measured pebble radius to be comparable. According to Hertzian contact mechanics [5], all peak stresses within a pebble under a compressive load linearly scale with the maximum pressure p_0 which is given by equation (3), with the loading force F, the reduced Young's modulus of sapphire and the pebble E^* and the pebble radius R. Therefore this relationship can be used for normalization. All pebbles of a given diameter $D_{measured}$ are normalized to a diameter of 1000 μm according to equation (4).

$$p_0 = \frac{1}{\pi}\left(\frac{6FE^{*2}}{R^2}\right)^{\frac{1}{3}} \quad (3)$$

$$F_{c,normalized} = \left(\frac{1000\mu m}{D_{measured}}\right)^{\frac{2}{3}} F_{c,measured} \quad (4)$$

As moisture might change the mechanical behavior of the pebbles, prior to the testing, the pebbles are carefully dried in a vacuum furnace at 10 Pa and 150 °C. The crush load of single pebbles is determined with a universal testing machine, UTS 10T (class of accuracy 0.1). For the measurements, the pebbles are individually placed between two sapphire plates by vacuum tweezers.

The mechanical loading of the pebble is performed until a typical load drop for a yield point is detected by the measurement software, which does not necessarily mean a complete disintegration of the pebble. The measured load at the so-determined yield point is constituted as the crush load of the specific pebble. A total of 40 pebbles are analyzed in this way for each sample.

To analyze the statistical nature of the failing of the LMT containing pebbles, a Weibull analysis was performed by means of a maximum likelihood estimation [6] for each composition. In this analysis the most probable parameters of a two-parameter Weibull distribution, i.e. the Weibull modulus and the characteristic load, are determined. As each failure mode is primarily characterized by its Weibull modulus, this analysis can give insight into the active failure modes.

2.3. Other characterization techniques and equipment

The density of the samples is determined by helium pycnometry (Micromeritics AccuPyc 1330), thus their closed porosity can be deduced as quotient of measured to theoretical density, if the molar phase composition of all i phases x_i is known. The calculation of the theoretical density of multiphase phase pebbles, ρ_{mix} is given by equation (7) with the molar masses of the composing phases, M_i, and their densities, ρ_i.

$$\rho_{mix} = \frac{\sum_{i=1}^{n} x_i M_i}{\sum_{i=1}^{n} x_i \left(\frac{M_i}{\rho_i}\right)} \quad (7)$$

Table 1 details the theoretical densities of the raw materials and the anticipated phases that are to be synthesized according to the equations (1)–(2). The composition of LLTO in Table 1 is not exactly identical to the LLTO powder synthesized within this work, as the