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# Reprocessing of lithium orthosilicate breeder material by remelting

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## Abstract

For the reuse of ceramic breeder materials in fusion technology, the possibility to recycle these materials is a precondition and an important issue due to the high costs of $^6$Li-enriched materials and waste considerations. For lithium orthosilicate pebbles, fabricated by a melt-spraying process, the remelting was investigated, as it represents a facile reprocessing process without an additional recycling step. For this purpose, $Li_4SiO_4$ pebbles with a lithium content according to expected DEMO end-of-life burn-ups were fabricated and then remelted with an addition of lithium hydroxide hydrate to gain the composition of the usual reference material with a surplus of 2.5 wt% $SiO_2$. It could be demonstrated, that the remelting process does not deteriorate the properties of the pebbles.
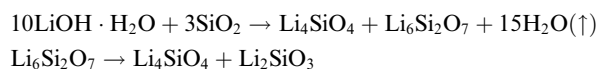© 2006 Elsevier B.V. All rights reserved.

## 1. Introduction

Slightly hyperstoichiometric lithium orthosilicate pebbles have been chosen as a possible breeder material for the European Helium Cooled Pebble Bed (HCPB) blanket [1]. This material has been developed in collaboration of Forschungszentrum Karlsruhe and Schott AG, Mainz [2]. The lithium orthosilicate ($Li_4SiO_4$, OSi) pebbles are fabricated by a melt-spraying technique in a semi-industrial scale facility. $Li_4SiO_4$ pebbles with a surplus of 2.5 wt% $SiO_2$ are produced by melting a mixture of lithium hydroxide hydrate and silica powders and then spraying the liquid material in air [3].

The sprayed glass droplets solidify during the flight and are collected as pebbles with different sizes, but only pebbles with a diameter in the range of 250–630 μm have been selected for the use as breeder material in the blanket. The yield of these pebbles is 50 wt% [4].

Because of the surplus of $SiO_2$, the resulting product is two-phase with $Li_4SiO_4$ as the main phase. The high-temperature phase $Li_6Si_2O_7$ as the minor part is obtained due to the rapid quenching of the melt. This phase is metastable at room temperature and decomposes during annealing to the thermodynamically stable phases lithium orthosilicate and lithium metasilicate ($Li_2SiO_3$) [5]. A thermal annealing ('conditioning') is usually performed before the pebbles are used in in-pile or out-of-pile experiments. The process can be represented by the following reactions:

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$$10\,LiOH \cdot H_2O + 3\,SiO_2 \rightarrow Li_4SiO_4 + Li_6Si_2O_7 + 15\,H_2O(\uparrow)$$
$$Li_6Si_2O_7 \rightarrow Li_4SiO_4 + Li_2SiO_3$$

Taking into account the large amounts of [6]Li-enriched breeder materials to be used in DEMO, a recycling of the material is essential due to cost and waste considerations. While ceramic breeder materials like lithium metatitanate, $Li_2TiO_3$, which are fabricated by a ceramic shaping or by sol–gel processes with subsequent sintering [6–9], require a complex wet chemical recycling process to obtain the [6]Li-containing raw material and to start a new fabrication process [8,10,11], ceramic pebbles fabricated by a melt process offer in principle the possibility to remelt residues or irradiated material.

The objective of this paper is the reprocessing of lithium orthosilicate pebbles by remelting and the investigation of any possible changes in the properties due to reprocessing. To investigate the recycling of OSi pebbles, it would be favourable to use irradiated material. However, due to the activation, no irradiated material could be used for the remelting, and only the chemical composition of pebbles expected at DEMO end-of-life relevant burn-ups was simulated. It was assumed that 50% [6]Li-enriched OSi pebbles will be used, and that a burn-up of 15% [6]Li will occur. Any changes in the microstructure like the development of pores and cracks observed e.g. in the EXOTHIC-8 irradiation experiment [12] had to be neglected. It is supposed, however, that any influence of the microstructure will be nullified by the melting process and the reprocessing will not be affected.
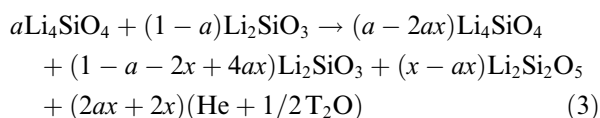
To calculate the change of the composition of the pebbles under irradiation, the loss of lithium due to the transmutation to tritium and helium has to be considered. Following [13], the reaction of lithium orthosilicate under irradiation can be represented by the following, here generalised reaction, where $x$ represents the actual fraction of burn-up with $0 \leqslant x \leqslant 0.5$ (e.g. a maximum of 100% burn-up of a 50% [6]Li-enriched material or 50% burn-up of a 100% enriched material):
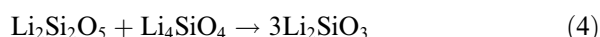
$$Li_4SiO_4 \rightarrow (1-2x)\,Li_4SiO_4 + 2x\,Li_2SiO_3$$
$$+ 4x(He + 1/2\,T_2O) \qquad (1)$$
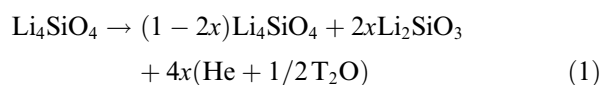
As OSi pebbles are a two-phase material, also the reaction of lithium metasilicate under irradiation has to be considered:

$$Li_2SiO_3 \rightarrow (1-2x)\,Li_2SiO_3 + x\,Li_2Si_2O_5$$
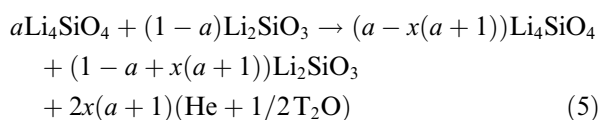$$+ 2x(He + 1/2\,T_2O) \qquad (2)$$
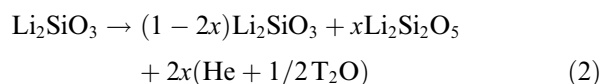
For a two-phase material with $a$ and $b$ representing the molar fraction of lithium orthosilicate and metasilicate, respectively, and with $a + b = 1$, we get the following reaction from (1) + (2):
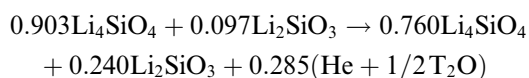
$$a\,Li_4SiO_4 + (1-a)\,Li_2SiO_3 \rightarrow (a - 2ax)\,Li_4SiO_4$$
$$+ (1 - a - 2x + 4ax)\,Li_2SiO_3 + (x - ax)\,Li_2Si_2O_5$$
$$+ (2ax + 2x)(He + 1/2\,T_2O) \qquad (3)$$

As long as the composition of the material lies within the two-phase region of lithium ortho- and metasilicate, $Li_2Si_2O_5$ will react with $Li_4SiO_4$ to form $Li_2SiO_3$:

$$Li_2Si_2O_5 + Li_4SiO_4 \rightarrow 3\,Li_2SiO_3 \qquad (4)$$

By using (4) in (3), the following reaction is obtained:

$$a\,Li_4SiO_4 + (1-a)\,Li_2SiO_3 \rightarrow (a - x(a+1))\,Li_4SiO_4$$
$$+ (1 - a + x(a+1))\,Li_2SiO_3$$
$$+ 2x(a+1)(He + 1/2\,T_2O) \qquad (5)$$

This reaction scheme is valid as long as both, the initial material and the irradiated material are within the two-phase region of lithium orthosilicate and metasilicate. Therefore the fraction of the burn-up $x$ has to fulfil the condition $x \leqslant a/(a+1)$. For the reference material with a surplus of 2.5 wt% $SiO_2$ and an assumed [6]Li-enrichment of 50%, the change in the phase composition after a [6]Li burn-up of 15% (i.e. $x = 0.075$) will amount to

$$0.903\,Li_4SiO_4 + 0.097\,Li_2SiO_3 \rightarrow 0.760\,Li_4SiO_4$$
$$+ 0.240\,Li_2SiO_3 + 0.285(He + 1/2\,T_2O)$$

Accordingly, the lithium metasilicate content will increase from 9.7 mol% in the reference material to 24.0 mol% in the material simulating 15% [6]Li burn-up. From the phase composition a target value of 6.4 wt% $SiO_2$ surplus can be calculated for these pebbles. From (5) it can also be deduced that 50% [6]Li-enriched OSi pebbles with the reference composition will remain two-phase under irradiation up to a [6]Li burn-up of nearly 95%.

## 2. Experimental

In a fabrication campaign several batches of lithium orthosilicate pebbles were produced by melt-spraying at Schott AG, Mainz. As costs have to be saved and the isotope ratio is not supposed to have any influence on the fabrication process or on the properties of the pebbles, the fabrication

was carried out with natural enriched lithium hydroxide hydrate (7.5 at.% $^6$Li). The yield of each batch amounted to approx. 700 g of pebbles in the diameter range 250–630 μm. While three batches were fabricated as reference material with the target value of 2.5 wt% $SiO_2$ surplus (sample OSi 06/1), three batches were produced aiming at a higher $SiO_2$ surplus of 6.4 wt%. The latter with an actual $SiO_2$ surplus of 6.1–7.5 wt%, were then remelted with additions of lithium hydroxide hydrate to gain the usual $SiO_2$ surplus of 2.5 wt% (sample OSi 06/3).

The characterisation was carried out on each batch, in the initial state as well as after conditioning at 970 °C for one week in air. The quality control of the different pebble batches was based on the following tests:

– Chemical analysis (Li and Si by Schott AG, impurities by inductively coupled plasma-optical emission spectrometry at FZK),
– phase analysis by X-ray powder diffraction,
– investigation of the microstructure by optical and scanning electron microscopy,
– measurement of density and porosity by Hg-porosimetry (three samples per batch) and He-pycnometry,
– measurement of the specific surface area by 1-point BET, and
– compressive crush load tests on 40 single pebbles with a diameter of 500 μm, previously dried at 300 °C.

As it is known, that the properties of OSi pebbles are slightly varying from batch to batch [4], the results for the different materials in Tables 1 and 2 are in each case given as mean values of three batches.

Table 1
Chemical characteristics of the reference material OSi 06/1 and the remelted material OSi 06/3

| | Reference material OSi 06/1 | Remelted material OSi 06/3 |
|---|---|---|
| $Li_2O$ (wt%) | $47.9 \pm 0.2$ | $48.4 \pm 0.2$ |
| $SiO_2$ (wt%) | $51.6 \pm 0.3$ | $51.4 \pm 0.2$ |
| $SiO_2$ surplus (wt%)[a] | $3.4 \pm 0.4$ | $2.7 \pm 0.5$ |
| C (wt%) | $0.06 \pm 0.00$ | $0.07 \pm 0.01$ |
| Al (ppm) | $21 \pm 4$ | $43 \pm 19$ |
| Co (ppm) | $<1$ | $<1$ |
| Pt (ppm) | $78 \pm 5$ | $107 \pm 11$ |
| *As-received* | | |
| $Li_4SiO_4$ (mol%)/(wt%)[a] | $85 \pm 2/76 \pm 3$ | $88 \pm 2/81 \pm 3$ |
| $Li_6Si_2O_7$ (mol%)/(wt%)[a] | $15 \pm 2/24 \pm 3$ | $12 \pm 2/19 \pm 3$ |
| *After conditioning* | | |
| $Li_4SiO_4$ (mol%)/(wt%)[a] | $87 \pm 2/90 \pm 1$ | $89 \pm 2/92 \pm 1$ |
| $Li_2SiO_3$ (mol%)/(wt%)[a] | $13 \pm 2/10 \pm 1$ | $11 \pm 2/8 \pm 1$ |

[a] Calculated from chemical analysis.

## 3. Results and discussion

The important chemical characteristics of the pebbles are summarised in Table 1. While the $SiO_2$ surplus of the reference material OSi 06/1 is higher than the target value of 2.5 wt%, the $SiO_2$ surplus of the remelted material OSi 06/3 agrees quite well with the target value. Consequently, the expected amounts of the high-temperature phase, $Li_6Si_2O_7$, in the initial material as well as the expected amounts of lithium metasilicate in the conditioned material are higher for the reference material, which was confirmed by X-ray diffraction. The variation of the $SiO_2$ surplus is caused by uncontrollable lithium losses during melting and spraying. Concerning the impurities, the remelted material exhibit a slightly higher content of aluminium than the reference material with an amount of 21 ppm. This is actually

Table 2
Physical characteristics of the reference material OSi 06/1 and the remelted material OSi 06/3

| | As-received | | After conditioning | |
|---|---|---|---|---|
| | Reference material OSi 06/1 | Remelted material OSi 06/3 | Reference material OSi 06/1 | Remelted material OSi 06/3 |
| Size distribution $d_{50}$ (μm) | $295 \pm 5$ | $305 \pm 10$ | n.a. | n.a. |
| Closed porosity (%)[a,b] | $0.6 \pm 0.0$ | $0.6 \pm 0.1$ | $0.5 \pm 0.1$ | $0.7 \pm 0.0$ |
| Open porosity (%)[a,c] | $3.4 \pm 0.5$ | $3.6 \pm 0.5$ | $3.1 \pm 0.5$ | $3.0 \pm 0.4$ |
| Density (%TD)[a,c] | $95.5 \pm 1.5$ | $94.8 \pm 1.0$ | $95.2 \pm 1.0$ | $95.4 \pm 0.8$ |
| Specific surface area (m$^2$/g) | $0.20 \pm 0.03$ | $0.10 \pm 0.01$ | $0.11 \pm 0.01$ | $0.10 \pm 0.02$ |
| Crush load (N) | $7.0 \pm 1.2$ | $7.2 \pm 1.6$ | $5.7 \pm 1.7$ | $6.6 \pm 1.0$ |

[a] A density of 2.4 g/cm$^3$ was assumed as theoretical density.
[b] Calculated from the inner density measured by He-pycnometry.
[c] Measured by Hg-porosimetry.

only caused by an, at present unexplainable, higher Al content of 68 ppm of one remelted batch. As expected, the platinum content of the OSi 06/3 material seems to be increased by remelting. An increase in the Pt content should have no negative effect on the function of ceramic breeder materials, since platinum is even suggested as a catalyst to enhance the tritium release [14]. Impurities of <35 ppm Al and 1–2 ppm Co are usually obtained with the currently used raw materials [3]. (Since the Pt crucible is supposed to represent the only source of contamination in the melt-spraying process, the impurities of the product – with the exception of Pt – solely depend on the impurities of the raw materials.) The amounts of aluminium and cobalt are an important factor for the recycling process, as they dominate the activation of the irradiated material. Based on a higher amount of impurities for OSi pebbles fabricated from different raw materials, a waiting period of 50–100 years for hands-on recycling of OSi pebbles was previously calculated for 60 ppm Al and 4 ppm Co [15]. As Co is the major contributor at times less than 50 years, a reduction of the Co content would result in shorter waiting periods for the recycling if remote handling is adopted.

The morphology and surface appearance of the different pebble batches are very similar. Most of the pebbles are well spherically shaped, but in some cases smaller pebbles, which were captured during the flight, stick to the surface of a larger pebble (Fig. 1). The majority of the surfaces of the reference and as well as of the remelted pebbles exhibits the known dendritic solidification microstructure of $Li_4SiO_4$ due to heterogeneous nucleation [16] (Fig. 2). The reference and the remelted pebbles reveal at cross-sections a characteristic amount of cracks and pores, caused by the rapid quenching and the difference in density between the amorphous and the crystallised state of about 6% (based on room temperature measurements of [17]). Additional cracks may occur, when the cooled pebbles bounce against the metallic collecting container in the fabrication facility [2]. Furthermore, in each batch some pebbles with large cavities or large open pores can be detected that are caused by air inclusions entrapped in the melt droplets during the spraying process. The dendritic microstructure at etched cross-sections is very similar in case of the reference and the remelted material (Fig. 3). The high-temperature phase, $Li_6Si_2O_7$ (light grey), with a lower peritectic temperature is embedded in the $Li_4SiO_4$ dendrites (dark grey).

The pebble size distributions of all batches displayed a $d_{50}$ value of about 300 μm with the maximum asymmetrically shifted to lower pebble sizes. This asymmetric distribution is caused by screening the pebbles to the desired sizes of 250–630 μm. A density of 94–96%TD and an open porosity of 3–4% were detected for all batches by Hg-porosimetry,
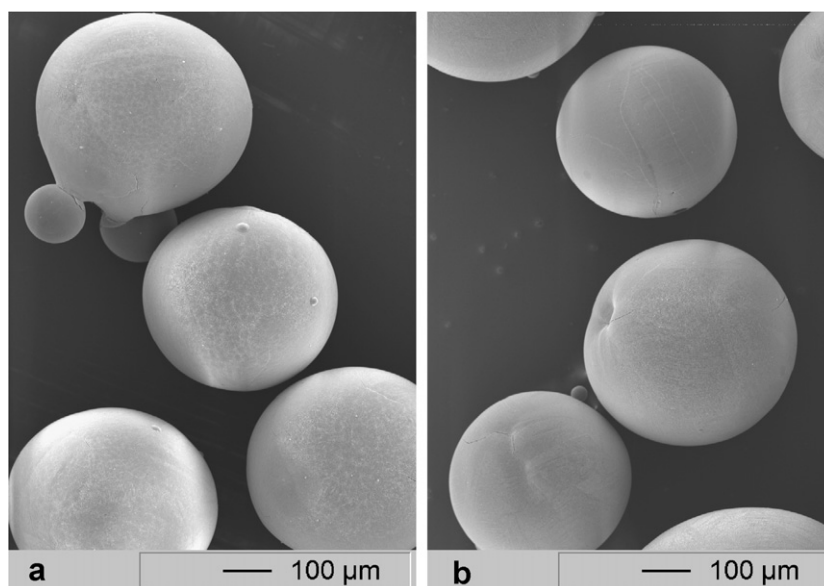


Fig. 1. Morphology of (a) the reference pebbles and (b) the remelted pebbles, both in the as-received state (SEM).
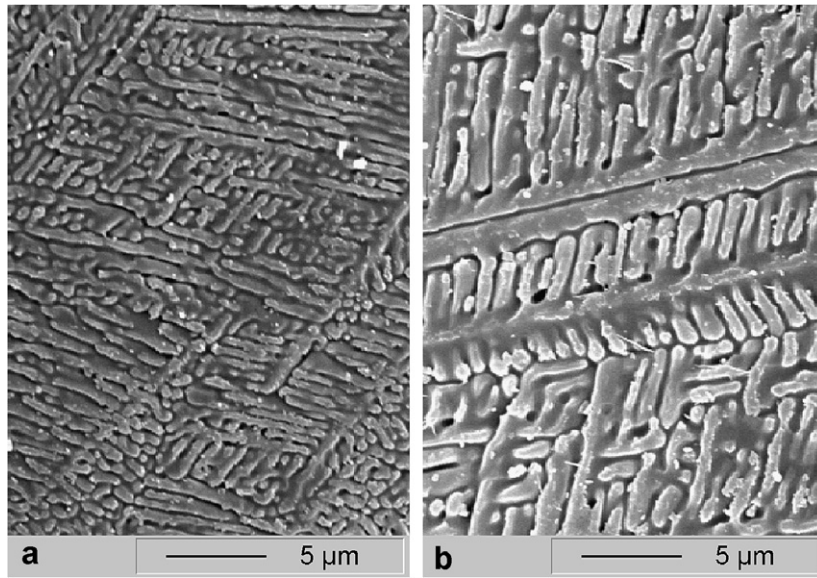
Fig. 2. Surface appearance of the as-received pebbles with a dendritic solidification microstructure of $Li_4SiO_4$: (a) the reference pebbles and (b) the remelted pebbles (SEM).
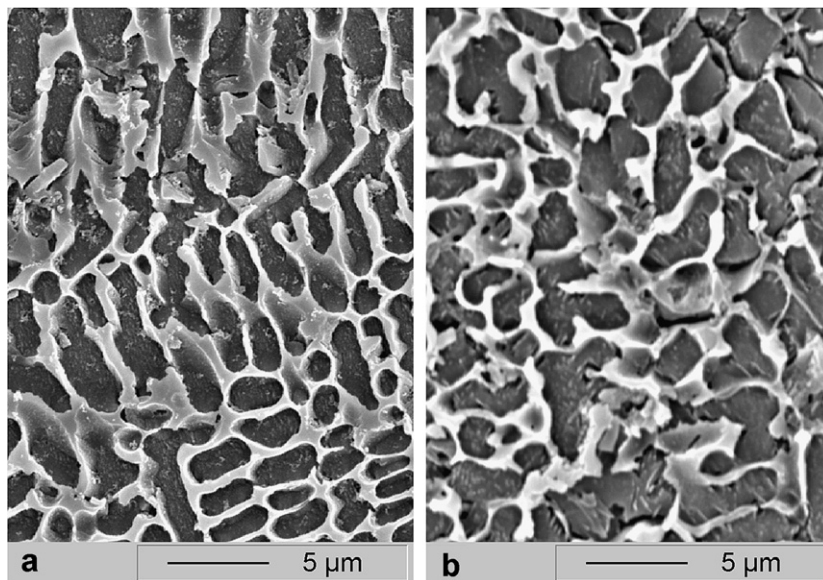


Fig. 3. Microstructure in the as-received state at etched cross-sections: (a) the reference material and (b) the remelted material. The high-temperature phase $Li_6Si_2O_7$ (light grey) is embedded in the $Li_4SiO_4$ dendrites (dark grey) (SEM).

while the closed porosity measured by He-pycnometry amounts to less than 1% in all cases (Table 2). The standard deviation of the density measured by Hg-porosimetry is quite large, and this method is afflicted by errors, as it is very difficult to distinguish between the intrusion of voids between the pebbles and the intrusion of the first pores at low pressures. To make sure that all voids between the pebbles were filled with mercury, three low-pressure cycles were performed before the final run was started. That means that pores near the surface with openings larger than 5 µm may be filled in the low-pressure cycle and are not detected as open porosity.

The specific surface area of untreated OSi pebbles is usually $0.2 \, m^2/g$ [3], as detected for the reference material. The value of $0.1 \, m^2/g$ for the remelted material is slightly lower than usual, but similar values were previously measured as well [4]. The crush load of the reference and the remelted material amounts to 7 N with large deviations of the mean values. The variations may be explained by different amounts of cracks and different crack orientations in the pebbles to the normal force of the crush load.

During conditioning the high-temperature phase, $Li_6Si_2O_7$, is decomposed, and the dendritic microstructure is changed into a typical sintering microstructure. At the pebble surface, now grains of lithium metasilicate can be observed (Fig. 4). Due to the higher surplus of $SiO_2$ of the reference material, the amount of $Li_2SiO_3$ grains seems to be more pronounced in this case. The examination of cross-sections reveals that $Li_2SiO_3$ inclusions with a grain size of about 2 µm are mostly located at pores and grain boundaries, but there are also some smaller granular inclusions (Fig. 5). The grain size of $Li_4SiO_4$ amounts to approx. 10 µm after the conditioning. Simultaneously with the change of the microstructure, a rearrangement and coarsening of pores take place.

The density of 95%TD and the porosities are not significantly altered by the conditioning (Table 2). In case of the remelted material, the conditioning seems to have a 'post-sintering' effect, as the density is slightly increased. The surface area now amounts to $0.1 \, m^2/g$, the usually observed value for conditioned batches. The decrease of the surface area is caused by the change of the microstructure, i.e. the disappearance of the dendritic structure, which leads to a less rough surface on the micrometer scale. The crush load is somewhat lowered to about 6 N by the conditioning with a similar large scattering as in case of the untreated materials.

The reference and the remelted material exhibit very similar, satisfactory properties, and display a good reproducibility of this fabrication campaign. The variation between different batches of the same material, displayed by the scattering of values, is similar to or even larger than the difference between the reference and the remelted material. That means that lithium orthosilicate pebbles fabricated by melt-spraying can simply be reprocessed by remelting without any additional recycling step. A remelting is highly advantageous as any wet chemical process would involve huge amounts of chemicals. Based on the details given in [10,11] and depending on the chemical route proposed, an amount of 12–20 l of solvent is necessary solely for the dissolution step of only 1 kg of lithium metatitanate. Fig. 6 illustrates the different reprocessing routes proposed for ceramic breeder materials in case of a melting process for $Li_4SiO_4$ (left) and in case of a ceramic shaping process with subsequent sintering for
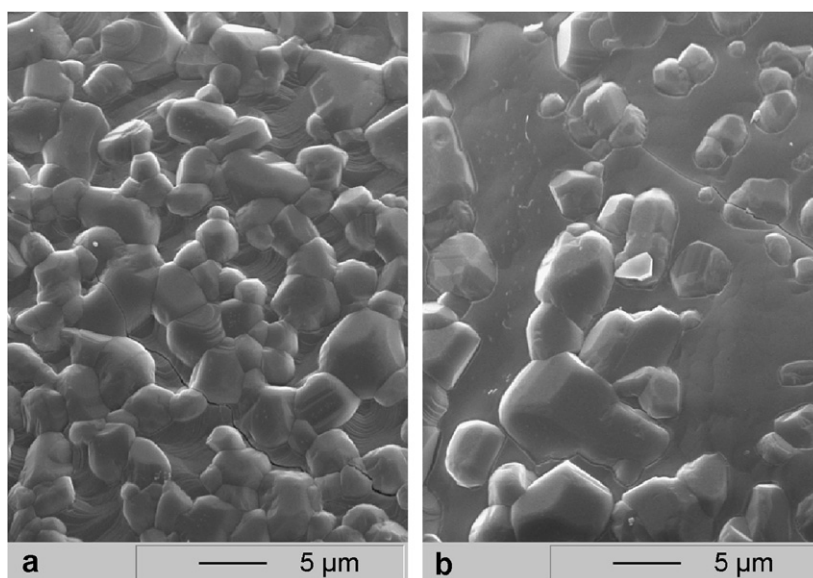


Fig. 4. Surface of the pebbles with $Li_2SiO_3$ grains after conditioning: (a) the reference pebbles and (b) the remelted pebbles (SEM).
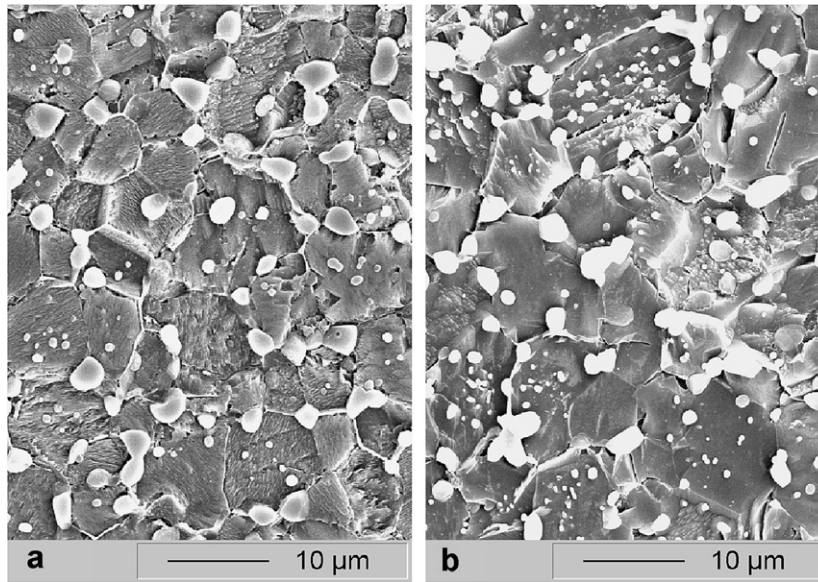
Fig. 5. Microstructure after conditioning at etched cross-sections: (a) the reference material and (b) the remelted material. $Li_2SiO_3$ inclusions (light grey) are mostly located at pores and the grain boundaries of $Li_4SiO_4$ (dark grey) (SEM).
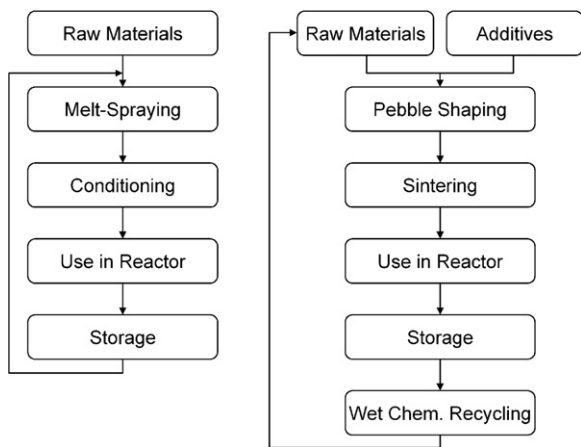


Fig. 6. Schematic representation of the different reprocessing routes for lithium orthosilicate pebbles fabricated by melt-spraying (left) and lithium metatitanate pebbles fabricated by a shaping and sintering process (right).

$Li_2TiO_3$ (right). Due to the activation under irradiation, in both cases the material will have to be stored for a certain waiting period before the reprocessing can be started.

## 4. Conclusions

The reprocessing of lithium orthosilicate pebbles was investigated by remelting. For this purpose, pebbles with a higher $SiO_2$ surplus were fabricated to simulate the chemical composition of pebbles with DEMO end-of-life relevant burn-ups. These pebbles were remelted with additions of lithium hydroxide hydrate to obtain pebbles with the composition of the usual reference material. It was demonstrated that properties and microstructure of the pebbles are not influenced by remelting, and that the remelted pebbles meet the demands of the HCPB blanket, like density and crush load, in the same way as the reference material. For pebbles fabricated by melt-spraying, no time- and cost-consuming additional wet chemical process step is necessary to recycle the expensive [6]Li isotope. However, it is not possible to remove any activated impurities by remelting of irradiated pebbles. To reduce the waiting period for the recycling process, it is aimed at the use of ultra pure raw materials. The additional costs of these materials should easily be compensated by a shorter waiting period and the less expensive reprocessing.

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