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Crystallisation and microstructure of lithium orthosilicate pebbles

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Abstract

Slightly overstoichiometric lithium orthosilicate (Li_4SiO_4) pebbles are fabricated by a melt-spraying process, where the droplets are rapidly quenched to room temperature. Depending on their size, the solidified pebbles exhibit different microstructures. While the crystallised pebbles always display some pores and cracks, the amorphous ones are mostly free of any defects. The crystallisation process of amorphous pebbles was therefore investigated to decrease the amount of cracks and pores with the aim of improving the mechanical properties of the final product. The development of phases during crystallisation was studied by thermoanalysis, X-ray diffraction and electron microscopy. The crystallisation takes place in three steps. At about 300–350 °C an unidentified, intermediate phase is nucleated. In a second step the formation of Li_4SiO_4 takes place at about 500 °C, while lithium metasilicate (Li_2SiO_3) is the last phase to appear at temperatures above 600 °C.

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1. Introduction

Lithium orthosilicate and lithium metatitanate have been chosen as alternative tritium breeder materials for the European helium cooled pebble bed (HCPB). Slightly overstoichiometric lithium orthosilicate (Li_4SiO_4) pebbles have been developed in close cooperation with Schott AG (Mainz, Germany). They are fabricated by a melt-spraying process in a pilot plant that allows for a production of 200–300 kg/year. Li_4SiO_4 pebbles with a surplus of SiO_2 are produced by melting LiOH and SiO_2 [1]. Droplets are generated from the flowing melt by an air jet and solidify during the flight. The pebbles gathered in a collecting container have diameters up to about 1 mm, but only the pebbles ranging from 250 to 630 μm with an yield of about 50 wt% are usually used for characterisation and further experiments [2].

Because of the surplus of SiO_2, the resulting product is two-phase with Li_4SiO_4 as the main phase. As the minor phase, the high-temperature phase $Li_6Si_2O_7$ is obtained due to the rapid quenching of the melt. This high-temperature phase is metastable at room temperature and decomposes during annealing to the thermodynamically stable phases lithium ortho- and metasilicate (Li_2SiO_3) [3].

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The process can be represented by the following reactions:

$$10LiOH + 3SiO_2 \Rightarrow Li_4SiO_4 + Li_6Si_2O_7 + 5H_2O(\uparrow),$$
$$Li_6Si_2O_7 \Rightarrow Li_4SiO_4 + Li_2SiO_3.$$

The majority of the pebbles is crystallised and appears pearly white, but a small amount of glassy pebbles can also be observed. While the crystallised pebbles always exhibit some cracks and pores, the amorphous pebbles are mostly free of any defects. Since cracks and pores affect the mechanical properties of the breeder material, a well controlled crystallisation of amorphous material could lead to an improvement of the thermomechanical behaviour of the pebble bed. The crystallisation behaviour of the amorphous pebbles was therefore investigated with the aim of inducing crystallisation with a minimum of cracks. A modified production process with a higher yield of amorphous pebbles in the desired range of 250–630 μm and a subsequent controlled heat treatment may then open the possibility for an improved breeder material.

2. Materials and methods

The pebble batch used for the experiments was produced by the melt-spraying process and had a composition of 48.3 wt% Li_2O and 51.4 wt% SiO_2, corresponding to molar phase compositions of 87.6% Li_4SiO_4 and 12.4% $Li_6Si_2O_7$ or 88.9% Li_4SiO_4 and 11.1% Li_2SiO_3, respectively. The amount of impurities of 0.3 wt% was mainly attributed to carbon due to absorbed CO_2, and impurities of the raw materials. The batch was screened to obtain a fraction of pebbles with diameters smaller than 50 μm. Pebbles screened to a diameter of 500 μm were used in some experiments for comparison.

Thermoanalytical experiments were performed by simultaneous TG/DSC (thermal gravimetry/differential scanning calorimetry) (STA 449 C Jupiter, Netzsch) under air with a heating rate of 10 K/min. Pebbles with diameters <50 μm were heated at 10 K/min to different temperatures in a furnace under air and then removed from the hot furnace to be quenched to room temperature. Additional samples were heat treated with different heating rates and dwell times. The microstructure was studied on polished and etched cross-sections by SEM (scanning electron microscopy) (JSM 6400, Jeol). The phase composition was investigated at room temperature by X-ray powder diffraction (D 5005, Bruker-AXS; CuKα radiation, sample rotation).

3. Results and discussion

Depending on their size and cooling history, three different microstructures can be found in the pebbles as received from the producer. The majority of the pebbles is characterised by a dendritic solidification microstructure of Li_4SiO_4 with small inclusions of $Li_6Si_2O_7$ (Fig. 1(a)). This microstructure is assumed to be caused by heterogeneous nucleation at pores, cracks and impurities, or by collision of pebbles during flight. Some, mostly medium-sized pebbles exhibit a microstructure of smaller, granular orthosilicate grains and small inclusions of $Li_6Si_2O_7$, that suggests a homogeneous nucleation (Fig. 1(b)). Due to the extremely rapid cooling, small pebbles, however, solidify amorphously. The ratio between amorphously solidified and crystallised pebbles increases with decreasing pebble size. The probability of heterogeneous nucleation sites, introduced e.g. by pores or collision of pebbles, decreases with decreasing size of the droplets. If no heterogeneous nucleation sites are present, the size-dependent cooling rate determines whether homogeneous nucleation or amorphous solidification will occur in the pebbles. The pebbles <50 μm used for the experiments are transparent and optically amorphous and do not display any defects in contrast to the crystallised pebbles (Fig. 2). It should be noted that even in this pebble fraction a small percentage of pebbles is crystallised due to heterogeneous nucleation.

The thermal analysis performed on well crystallised pebbles with a diameter of 500 μm reveals three exothermic reactions between 600 °C and 750 °C during heating and the corresponding endothermic peaks between 580 °C and 730 °C during cooling (Fig. 3(a)). While all three peaks at about 615/595 °C, 665/645 °C and 735/715 °C have previously been observed by thermoanalysis and are supposed to be caused by polymorphic transitions of Li_4SiO_4 [4], Kleykamp did not observe the first peak at 615/595 °C and assumed it to be associated with recrystallisation effects [5]. In our experiments, these three reversible peaks were observed in cyclic heating experiments and even on samples treated at 970 °C for 1 week. Therefore recrystallisation effects can definitely be ruled out and the assumption of a phase transformation seems to be more likely. In addition, cyclic heating experiments of the large

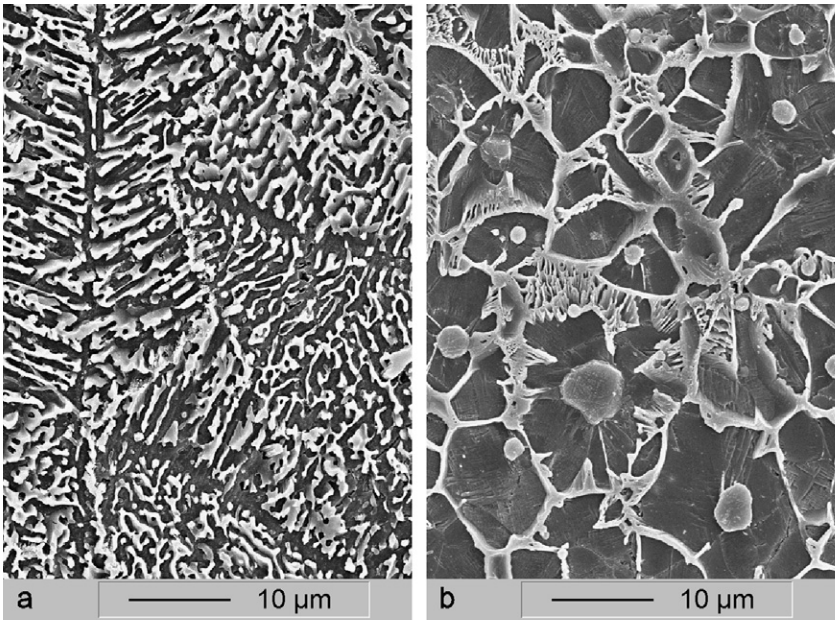

Fig. 1. Different microstructures observed at cross-sections of crystallised pebbles, that are due to (a) heterogeneous and (b) homogeneous nucleation (SEM). The main phase Li_4SiO_4 appears dark grey, $Li_6Si_2O_7$ inclusions are light grey.

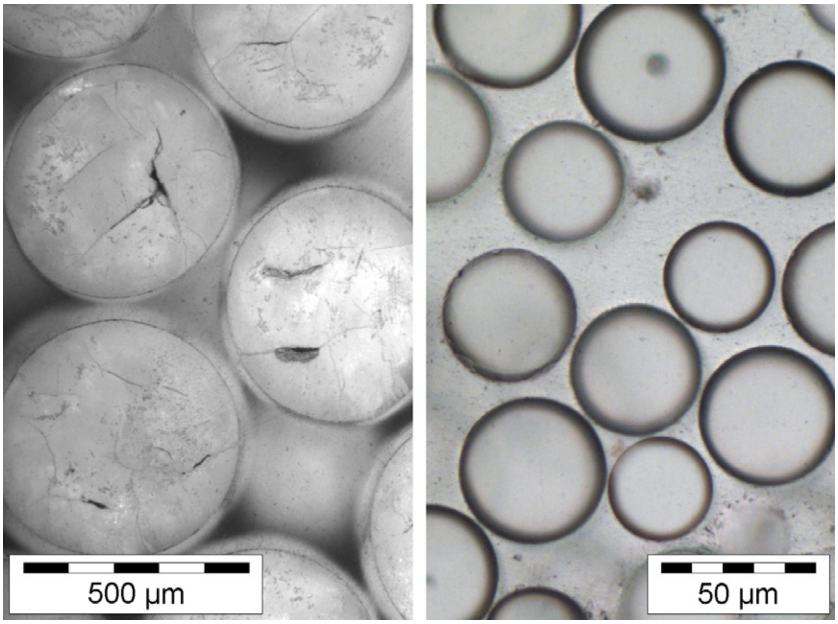

Fig. 2. Optical micrographs of the large pebbles (left) and of pebbles with diameters <50 µm (right).

pebbles revealed no difference in the heat flow between the first and the subsequent heating cycles. Hence, it can be assumed that the heat flow of the decomposition of the small amount of the high-temperature phase, $Li_6Si_2O_7$, is too small to be detected. The thermogravimetry displays a total weight loss of about 0.7 wt% in three steps, which is assumed to be due to the release of absorbed water and carbon dioxide from the pebbles' surface. Kato et al. found that carbon dioxide and water are easily absorbed by lithium orthosilicate even from ambient air at room temperature [6]. During heating they

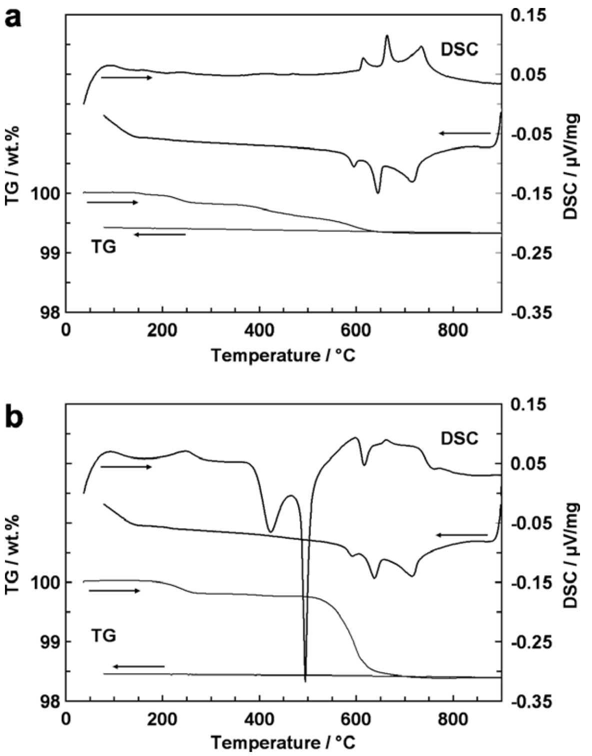

Fig. 3. Thermoanalysis of pebbles with (a) a diameter of 500 µm, and (b) diameters <50 µm (↑ endothermic, ↓ exothermic).

observed the release of water in the temperature range of 150–250 °C, while CO_2 was mainly detected between 400 °C and 520 °C.

The thermoanalysis performed on pebbles with diameters <50 µm, i.e. predominantly amorphous pebbles, displays three distinctly exothermic reactions with peak temperatures of 423 °C, 494 °C, and 616 °C, as well as two small endothermic peaks at 247 °C, and 663 °C during heating (Fig. 3(b)). Additional endothermic reactions can be deduced at temperatures of about 600 °C and 730 °C. During cooling, the small pebbles exhibit a heat flow almost identical to the large pebbles. Comparing the observed heat flows of both samples, it is apparent that the 3 exothermic peaks during heating of the small pebbles should be caused by crystallisation or phase formation processes. While the endothermic reactions at 663 °C and ~730 °C are in agreement with the polymorphic transitions of Li_4SiO_4, the endothermic reactions at 247 °C and ~600 °C correspond to steps in the weight loss of 0.2 wt% and 1.4 wt%, respectively. Experiments with pebbles of different sizes displayed an increasing weight loss with decreasing size, i.e. increasing specific surface area of the pebbles. Thus the higher weight loss observed in the smaller pebbles may just be caused by the higher surface area. In case of the 50 µm pebbles, experiments by coupled TG–FTIR (Fourier transform infrared spectroscopy) proved the release of H_2O in the temperature range of 150–300 °C as well as between 500 °C and 700 °C. In addition, CO_2 was determined in the temperature range of 500–600 °C.

The X-ray diffraction pattern obtained from samples quenched from various temperatures are shown in Fig. 4. Due to a small amount of crystallised pebbles in the used pebble fraction <50 µm, small peaks of lithium orthosilicate appear in all samples treated at temperatures up to 475 °C. Furthermore, minor traces of lithium carbonate, Li_2CO_3, were found in samples up to a temperature of 505 °C. Apart from this fact, the first crystallisation in the amorphous pebbles occurs in the sample treated at 350 °C (Fig. 4, lower part). The intensity of this unidentified phase increases with increasing temperature up to 450 °C. In the temperature range of 505–650 °C the peak positions are each more and more shifted to the nearest peak of lithium orthosilicate (Fig. 4, upper part). While the intensities of the orthosilicate peaks are noticeably increased at 505 °C, the first peaks for metasilicate can be observed at 650 °C.

From the results obtained by thermoanalysis at heating rates of 10 K/min and X-ray diffraction of quenched samples, it can be deduced that the nucleation of the unidentified phase occurs at $T > 300$ °C and is associated with the exothermic peak at 423 °C. Studying the crystallisation kinetics of very similar glasses, Wondraczek et al. measured

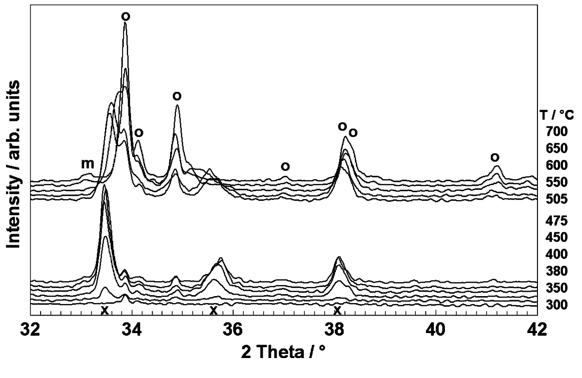

Fig. 4. Details of X-ray powder diffraction pattern of samples quenched from different temperatures, lower part: 300 °C, 350 °C, 380 °C, 400 °C, 450 °C, 475 °C, and upper part: 505 °C, 550 °C, 600 °C, 650 °C, 700 °C (Kα_2 corrected) (x = unidentified phase; o = orthosilicate; m = metasilicate).

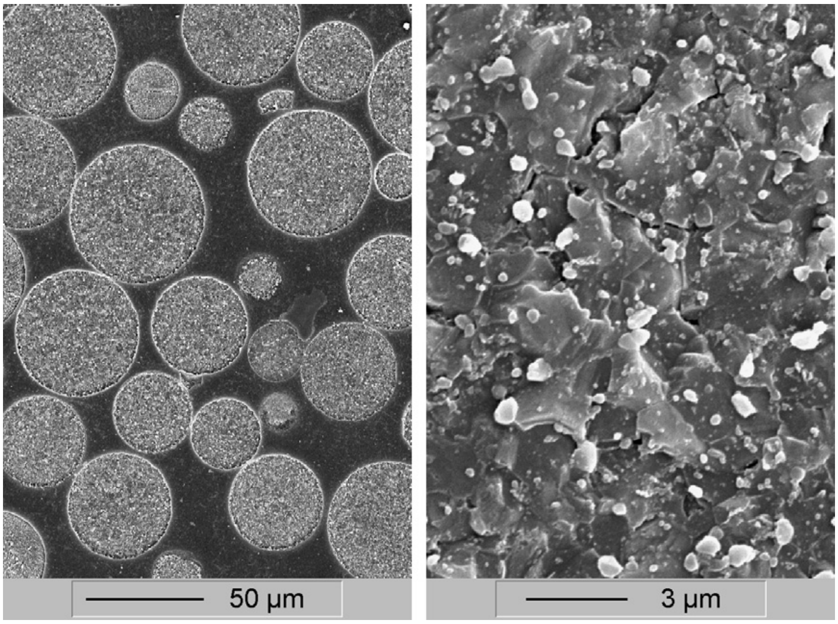

Fig. 5. Fine grained microstructure of lithium orthosilicate (dark grey) with inclusions of metasilicate (light grey) obtained after a heat treatment of amorphous pebbles at 800 °C for 72 h (SEM).

an activation energy of 90 kJ/mol for the formation of this phase [7]. The phase can be indexed on a hexagonal basis with $a_0 = 3.088(1)$ Å, $c_0 = 5.023(2)$ Å (obtained by Rietveld-refinement on a sample treated at 350 °C for 70 h). Systematic extinctions are compatible with a number of space groups, among them $P\ 6_3mc$ or $P\ 6_3/mmc$, but the small number of observed reflections (seven lines between 25° and 90° 2θ) along with the presence of other phases (Li_4SiO_4, Li_2CO_3) prohibits any reliable space group assignment. The powder pattern has some similarities to that of a lithium silicon oxynitride, Li_5SiNO_3, that has previously been observed in solid state reactions [8]. In our case, however, an oxynitride seems to be unlikely, as no nitrogen or NO_x was observed in coupled TG–FTIR measurements. The shifting of the peak positions at $T >$ 500 °C indicates a decrease of a_0 and an increase of c_0. At present it is unknown whether this shift is caused by an ordering mechanism or by a change in the chemical composition and if this is in some way correlated with the continuous weight loss observed in the thermoanalysis.

Corresponding to the exothermic peak at 494 °C, the formation of Li_4SiO_4 is observed at $T > 500$ °C. It is assumed that the exothermic reaction at 616 °C is related to the reversible transition observed in the DSC measurements of crystallised pebbles at 615/595 °C and represents a transition to a stable modification of Li_4SiO_4 at $T > 600$ °C. The heat flow due to the nucleation of about 11 mol% of Li_2SiO_3 seems to be too small to be detected.

Using the knowledge of the phase formation process, different heat treatments were carried out with amorphous pebbles to induce crystallisation. Fig. 5 displays a homogeneous, fine grained microstructure of lithium ortho- and metasilicate after a heat treatment at 800 °C for 72 h with intermediate dwell steps at 350 °C and 450 °C. The pebbles were still translucent after the heat treatment and revealed only very few small cracks introduced by the crystallisation.

4. Conclusions

Most of the lithium orthosilicate pebbles fabricated by the melt-spraying process are crystallised due to either heterogeneous or homogeneous nucleation and exhibit cracks, which are 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 [7]). The investigation of the crystallisation of the amorphous material allowed for an optimisation of the heat treatment to induce the formation of phases without introducing the usual amount of cracks and pores and thus improving the mechanical properties of the pebbles.

To apply this procedure and to verify the improvement of the breeder material, the fabrication process has yet to be modified to gain a higher yield of amorphous pebbles in the diameter range of 250–630 μm. While homogeneous nucleation should quite easily be avoided by an even higher cooling rate of the droplets, it will be difficult to prevent the heterogeneous nucleation caused by entrapped air bubbles, impurities or by collision of pebbles. It has also to be considered that a more controlled crystallisation will lead to a higher density of the pebbles with a lower amount of open porosity, which may decelerate the release of tritium in subsequent applications.

Acknowledgments

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