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Journal of Nuclear Materials 307–311 (2002) 811–816

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Characterisation of ceramic breeder materials for the helium cooled pebble bed blanket

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Abstract

In the European helium cooled pebble bed (HCPB) blanket slightly hyperstoichiometric lithium orthosilicate ($Li_4SiO_4 + SiO_2$) and lithium metatitanate ($Li_2TiO_3 + TiO_2$) pebbles are considered as candidate ceramic breeder materials. Such ceramic breeder pebbles and pebble beds were investigated in different types of experiments carried out at Forschungszentrum Karlsruhe. In longterm annealing experiments (96 days at 970 °C in He + 0.1% H_2 atmosphere) the behaviour of the pebbles under DEMO blanket relevant conditions was investigated. Mechanical uniaxial and triaxial compression tests at temperatures up to about 850 °C were performed to determine the mechanical behaviour of pebble beds as a function of temperature (stress–strain dependence, thermal creep behaviour, friction coefficients). Thermal conductivity measurements up to about 800 °C were carried out with the aim to study the effect of creep on the pebble bed heat conduction. An overview of the experimental activities on ceramic breeder materials is given.

1. Introduction

In the development of the European helium cooled pebble bed (HCPB) blanket pebbles of slightly hyperstoichiometric lithium orthosilicate ($Li_4SiO_4 + SiO_2$), density = 96–98% theoretical density (TD of Li_4SiO_4: 2.40 g/cm^3) and diameters in the range of 0.25–0.63 mm, produced by the melting-spraying method and of slightly hyperstoichiometric lithium metatitanate ($Li_2TiO_3 + TiO_2$), density = 86% (TD of Li_2TiO_3: 3.45 g/cm^3) and diameters in the range of 0.9–1.2 mm, produced by the extrusion-spheronization-sintering method are considered as candidate ceramic breeders.

At Forschungszentrum Karlsruhe, different types of experiments have been carried out to study the thermal and mechanical behaviour of ceramic breeder pebbles and pebble beds:

- long-term annealing experiments, to study the behaviour of pebbles under DEMO blanket relevant temperature and atmosphere;
- uniaxial compression tests (UCTs) at temperatures up to 850 °C to determine the mechanical characteristics of pebble beds (stress–strain dependence during stress increase and decrease, thermal creep strain at constant stress levels);
- triaxial compression tests (TCTs) to determine the friction coefficients of pebble beds necessary to describe the flow of pebbles in blanket elements;
- thermal conductivity measurements of pebble beds with the hot wire method. Tests in helium and air atmosphere and temperatures up to 800 °C were performed. In particular, the effect of thermal creep on the thermal conductivity was investigated.

Results from these experiments are reported and discussed.

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0022-3115/02/$ - see front matter
PII: S0022-3115(02)00983-2

2. Long-term annealing of Li_4SiO_4 pebbles

The long-term behaviour of Li_4SiO_4 and Li_2TiO_3 pebbles at HCPB-blanket relevant temperature and atmosphere (He + 0.1 vol.% H_2) was studied in long-term aging experiments carried out at FZK [1,2]. An operation time of 20 000 h and a maximum nominal temperature of about 900 °C in the front part of the DEMO blanket were assumed as reference. In order to have relevant results in less than 20 000 h, a temperature higher than 900 °C was used. Choosing 96 days experiment duration, an aging temperature of 970 °C was calculated assuming the creep process as the most important phenomenon at the maximum nominal temperature. The aging was performed in an oven consisting of Al_2O_3 tubes ($\varnothing = 4$ cm), one tube for each material. At the inlets and outlets of each tube, the H_2O content in the purge flow (600 ml/h of He + 0.1 vol.% H_2 at 1080 mbar) was monitored because it could influence the interaction between reducing purge flow and ceramics. Different analyses were performed on samples at predetermined time intervals: the Li content of the pebbles was measured by atomic emission spectroscopy, X-ray diffraction was used to investigate the phase composition, electron (SEM) and optical microscopy provided us with information on the microstructure, density, porosity and specific surface area measurements were also performed. Changes in the mechanical stability were investigated by crush load tests.

In the following the results obtained with lithium orthosilicate pebbles will be presented, data on lithium metatitanate pebbles can be found in [2]. In the initial state the high-temperature phase $Li_6Si_2O_7$ is present in the pebbles together with Li_2SiO_3 and Li_4SiO_4. It is formed due to the rapid quenching in the production process. Before starting the aging, the Li_4SiO_4 pebbles were pre-annealed in air at 1000 °C for two weeks in order to decompose this high-temperature phase. Afterwards only Li_4SiO_4 as the major phase and Li_2SiO_3 as a second phase were present in the pebbles. Li_4SiO_4 pebbles had, in the initial state, a dendrite structure (Fig. 1), and cracks are present in the cross-section of the pebbles (Fig. 2). The pre-annealing at 1000 °C produced the largest changes in the microstructure with rearrangement of the void volume in round pores. The microstructural changes caused an increase in the roughness of the pebble surface (Fig. 3). The microstructure did not change significantly during aging, there was only diffusion of metasilicate through the material and, at the end, lithium metasilicate was mostly homo-

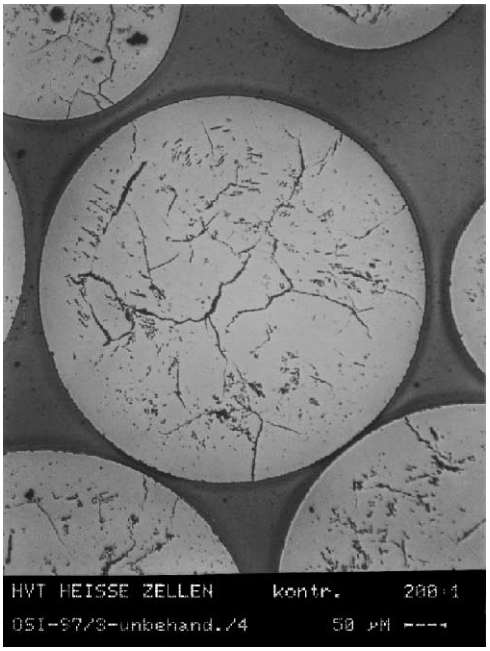

Fig. 2. Cross-section of Li_4SiO_4 pebbles before any thermal treatment (optical microscopy).

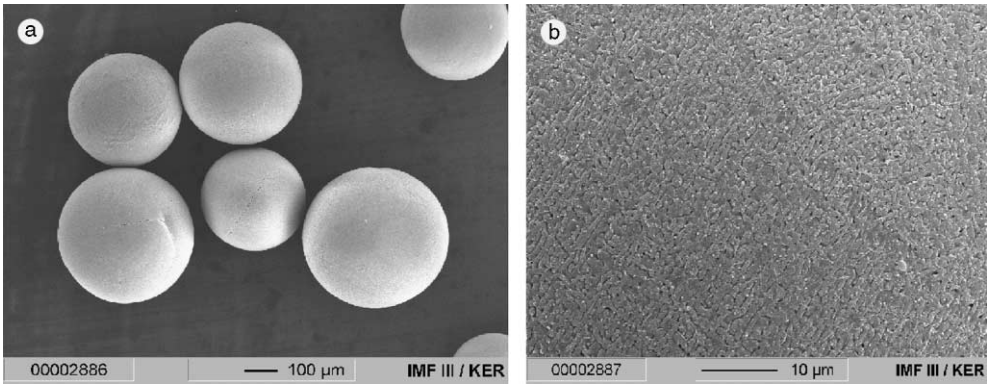

Fig. 1. Li_4SiO_4 pebbles in initial conditions (SEM): (a) pebbles, (b) pebble's surface detail.

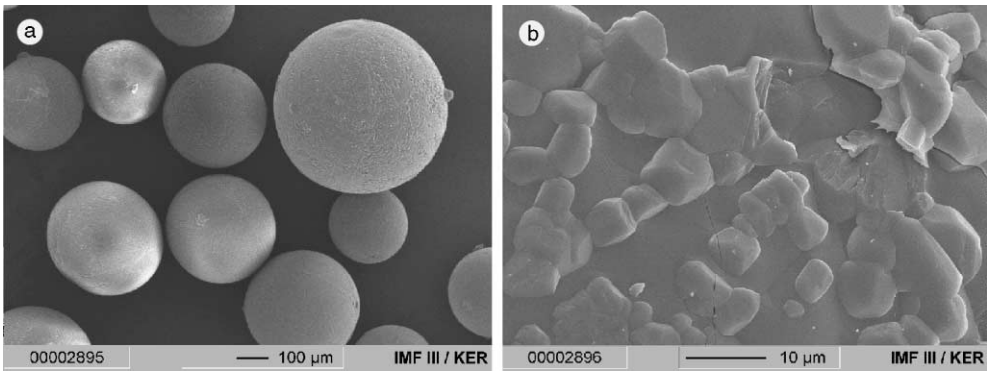

Fig. 3. Li_4SiO_4 pebbles after conditioning at 1000 °C (SEM): (a) pebbles, (b) pebble surface detail.

geneously distributed in the section with particles having dimensions between 1 and 4 μm (light gray particles in Fig. 4). Larger Li_2SiO_3 particles were present in microcracks and in the grain boundaries. Li_2SiO_3 reached the surface in some pebbles covering it with a layer of up to 10 μm thickness. In some cases, the surface layer of Li_2SiO_3 formed weak sintering necks between pebbles in contact. In the aging the purge flow reduced lithium orthosilicate pebbles which turned from white to light grey. According [3] impurities (e.g. Al, Fe) within the pebbles may make the reduction possible. The reasons for the change of colour have to be investigated in more detail. The density of the pebbles (He-pyknometry and Hg-porosimetry) remained practically constant during aging and the specific surface area (BET method) was reduced from about 0.2 to 0.1 m^2/g at the end of the experiment. No significant Li losses were observed. The mechanical stability of the pebbles was investigated by crush load tests on pebbles with $\emptyset = 0.5$ mm. In such tests a continuously increasing load is imposed by a piston to a single pebble until it breaks. According to the Hertz theory the shearing stress causing the failure of the pebble is located at the border of the contact surface between pebble and piston and is proportional to $(F/R^2)^{1/3}$, where F is the failure load, R the radius of the pebble, the proportionality coefficient is a function of the elastic properties of the materials used in the test. The larger the radius of the pebbles the larger will be the failure load. Lithium orthosilicate pebbles showed a reduction of the failure force from (8.9 ± 3.2) to (4.1 ± 1.8) N.

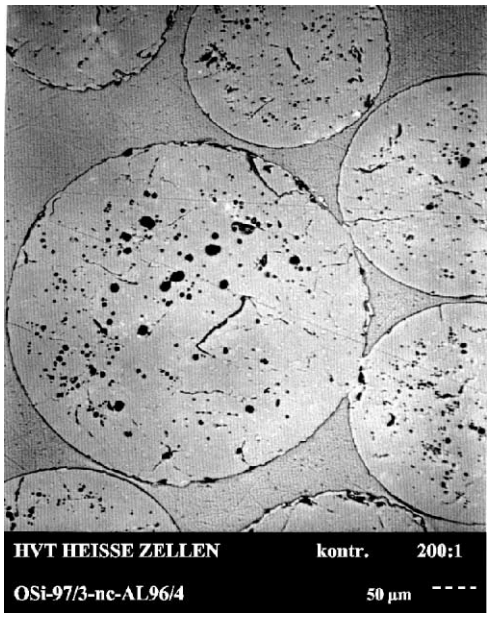

Fig. 4. Cross-section of Li_4SiO_4 pebbles after the 96 day aging (optical microscopy).

3. Thermomechanical tests on Li_4SiO_4 and Li_2TiO_3 pebble beds

The general practice to model the thermomechanical behaviour of pebble beds is to consider the granular material as a homogeneous medium applying the relevant methods extensively elaborated in soil mechanics. These methods require the knowledge of characteristic pebble bed properties, which are determined in standard tests such as:

1. UCTs,
2. TCTs.

3.1. Uniaxial compression tests

In UCTs the pebble beds contained in a cylindrical cavity are compressed in axial direction and the measured axial stress σ and axial strain ε are used to determine the modulus of deformation E of the pebble beds.

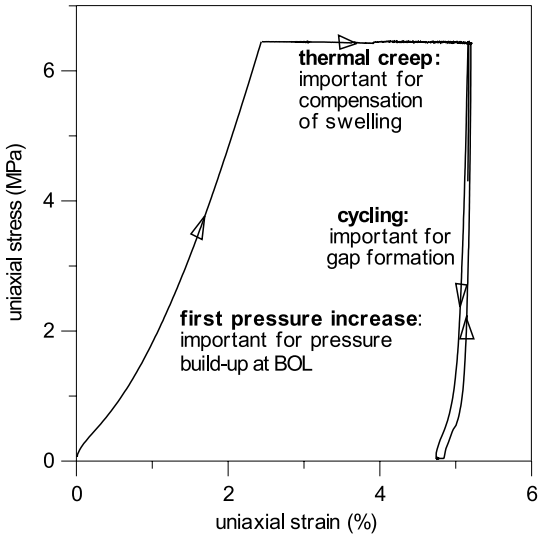

Fig. 5. UCT with a Li_2TiO_3 pebble bed at 750 °C.

UCT facilities are also used to establish correlations for thermal creep and Fig. 5 shows a characteristic UCT result for ceramic breeder pebble beds at elevated temperatures [4]: the first stress increase to a given value is governed by the irreversible displacement of particles forming a denser configuration, afterwards, keeping the maximum stress constant, the strain increases with time due to thermal creep. Cycling at the end of the creep period shows that the bed stiffness increases slightly due to the enlarged contact areas because of creep.

Extensive investigations with different ceramic breeder materials between ambient temperatures and 850 °C and pressures up to 8 MPa were performed [4–9]. An important part of the activity was the determination of the modulus of deformation for the first stress increase, being the experimental results for E generally fitted by an expression of the type

$$E = C\sigma^{m}. \tag{1}$$

The coefficient C is in general a function of temperature and also depends on the pebble bed packing conditions.

For the description of the bed-structure mechanical interaction the correlations for both the modulus of deformation (Eq. (1)) and the thermal creep are required as input. Due to the fact that thermal creep essentially causes the measured differences of the modulus of deformation between high and low temperatures, it is sufficient to use only the modulus of deformation at ambient temperature [5,6], therefore correlations were established [7] in which the coefficient C was expressed in terms of the packing factor γ (ratio of pebble volume to total volume) for orthosilicate and one type of metatitanate (CTI 1529 Ti1040 denominated as Ti-D was investigated in detail) at ambient temperature. For other types of metatitanates, values for C were determined for dense pebble beds (maximum achievable packing factors) [8].

A value of 0.45 for the exponent m in Eq. (1) fits well the data both for orthosilicate and all types of metatitanate pebble beds.

3.2. Thermal creep tests

Thermal creep is of significant importance for blanket breeder beds because it might reduce remarkably thermomechanical stresses after a few hours of operation [10] and might compensate the stress build-up due to irradiation induced swelling occurring during long-term operation. The proposed thermal creep correlation in integral form obtained from the experiments is

$$\varepsilon_{cr} = A' \exp(-B/T)\sigma^{n} t^{p}, \tag{2}$$

where ε_{cr} is the creep deformation, A' is in $((\mathrm{MPa})^{-n}\,\mathrm{s}^{-p})$, B and T in (K), σ in (MPa) and t in (s). Table 1 contains the corresponding values for A', B and the exponents n and p for orthosilicate pebbles and two types of metatitanate pebbles (developed by CEA and JAERI) which all are characterized by large grain sizes (10–50 μm) [6]. Recently, metatitanate pebbles (Ti-D) with smaller grain sizes (1–7 μm) were investigated in detail [8]: the Ti-D pebble beds often exhibit a second creep regime characterized by an increase of creep rates after about 100 min. Fig. 6 shows a comparison between beds of as manufactured Ti-D pebbles (grain size 1–2 μm) and of Ti-D pebbles (Ti-D lta) subjected, before the creep tests, to the aforementioned long-term annealing experiment, in which resulted in an increased grain size of about 50 μm.

3.3. Triaxial compression tests

An important quantity for the determination of the macroscopic movement of pebbles (particle flow) in blanket structures with inhomogeneous stress distributions is the inner friction angle β. This quantity can be obtained in TCTs, in which the granular material is compressed in a cylindrical cavity with a varying pressure p_1 in axial direction and a constant side pressure

Table 1
Coefficients for the thermal creep correlations [7]

Granular material-center	$\varepsilon_{cr} = A' \exp(-B/T)\sigma^{n} t^{p}$			
	A'	B	n	p
Li_4SiO_4-FZK	12.12	10 220	0.65	0.2
Li_2TiO_3 (lta)-CEA	0.67	7576	0.65	0.18
Li_2TiO_3-JAERI	0.37	6947	0.65	0.19

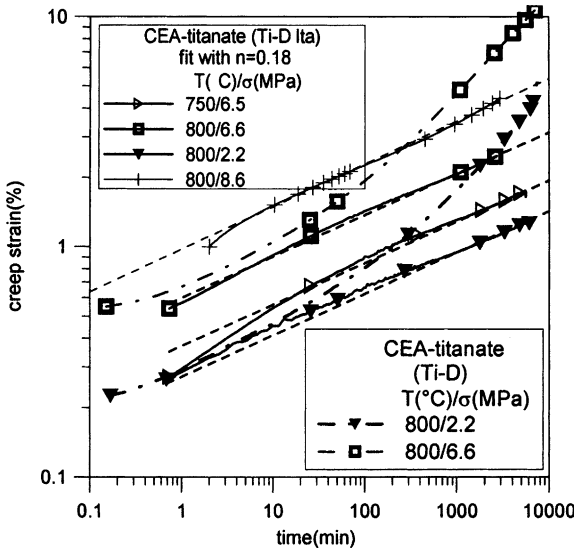

Fig. 6. Thermal creep strain in lithium metatitanate pebble beds.

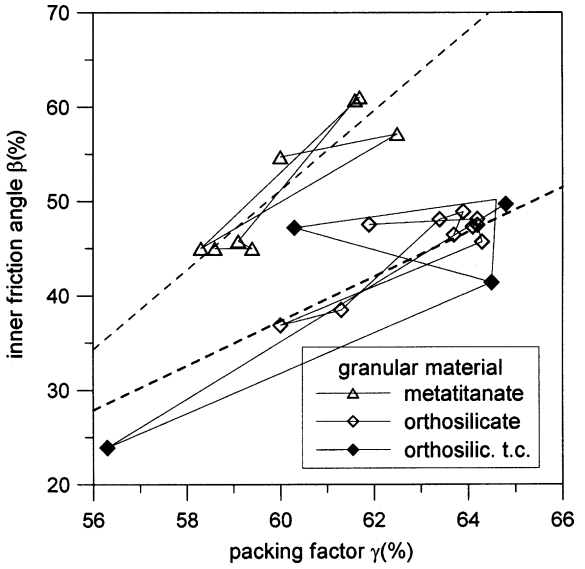

Fig. 7. Inner friction angle in pebble beds as a function of their packing factor.

p_2 perpendicular to the axis of the cylindrical cavity. Starting from the measured p_1 and p_2, β is calculated as:

$$\beta = \text{arctg}(3(p_1 - p_2)/(p_1 + 2p_2)). \quad (3)$$

The friction angle has been measured for lithium orthosilicate pebble beds (both annealed and not annealed pebbles) and for lithium metatitanate pebble beds. Fig. 7 shows β as a function of the packing factor γ. Taking into account the scattering of the data, practically the same $\beta(\gamma)$ fitting curve can be used for annealed and not annealed lithium orthosilicate pebbles. Lithium metatitanate pebbles have a larger friction angle than orthosilicate pebbles due to the larger nonsphericity and rougher surface.

3.4. Thermal conductivity measurements

For power reactor blankets the maximum temperatures in the breeder pebble beds are in the range of 900 °C. Because of different thermal expansions of the pebble beds and the structural material and irradiation effects, large compressive stresses might cause considerable plastic deformations of the pebbles and, for the proper thermomechanical blanket design, the knowledge of the thermal conductivity of deformed beds is of large importance. Very recently, the UCT facility described above was used to perform thermal conductivity measurements with the pulsed hot wire method [11]: a

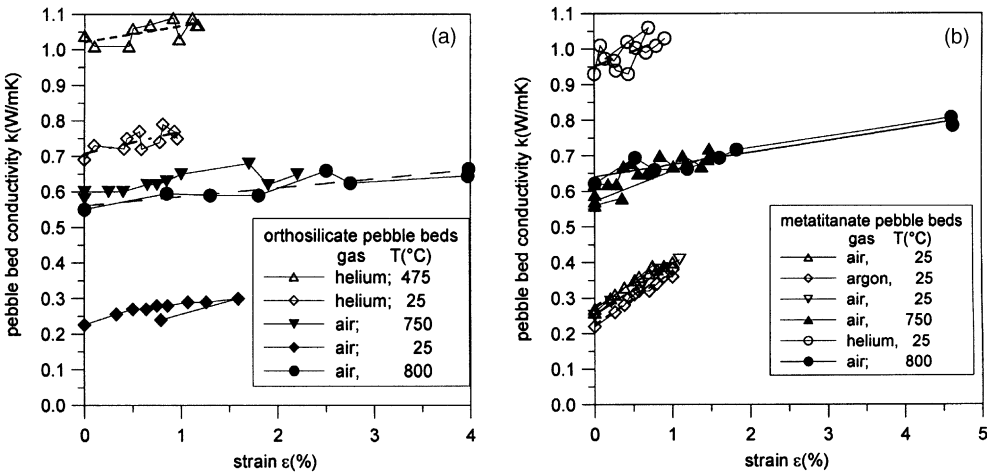

Fig. 8. Thermal conductivity in lithium orthosilicate (a) and lithium metatitanate (b) pebble beds.

standard technique for thermal conductivity measurement of poorly conducting materials. In these experiments the pebble bed is contained in a steel cylinder and has inside a long, thin electrical heater, which is connected to a power supply. The bed is heated in a furnace and, when its temperature reaches the steady state at a predefined value, the hot wire is switched on. On the basis of the measured time dependent hot wire's temperature increase, the effective thermal conductivity of the pebble bed can be calculated. Lithium metatitanate and orthosilicate pebble beds were investigated at temperatures up to 800 °C and bed deformations up to 4%. The measurements at high temperatures were performed in air, whereas also helium and argon were used in experiments at ambient temperature. Due to the low thermal conductivity of the investigated ceramic materials the increase of the thermal conductivity with increasing bed deformation is quite small and becomes negligible at high temperatures as shown in Fig. 8.

4. Conclusion

The behaviour of Li_4SiO_4 (microstructure, mechanical properties and Li-losses) in long-term annealing experiments simulating the maximum breeder temperature and the lifetime of the HCPB blanket (excluding irradiation effects) was found to be acceptable. In Li_4SiO_4 pebbles the pre-annealing at 1000 °C produced the largest changes in the microstructure. During the following aging process, the only significant change in the pebbles was the diffusion of lithium metasilicate in the material. Lithium metasilicate in some pebbles was emiched on their surface, covering it with a layer having a thickness of up to 10 μm. In some cases the surface layer of Li_2SiO_3 formed between pebbles in contact with sintering necks, which were weak and could be broken by modest mechanical actions. The lithium losses at 970 °C due to vaporisation were negligible. The mechanical stability of the pebbles (crush loads) was reduced in the pre-annealing stage and remained practically constant till the end of the aging. Nevertheless, the lower values are still acceptable in the blanket design.

In the frame of the development and characterisation of breeder pebble beds, also mechanical tests and measurements of the thermal conductivity at high bed deformation were performed at temperatures and pressures up to 850 °C and 8 MPa, respectively. In particular the measurements of the thermal conductivity showed that there are no distinct differences between lithium orthosilicate and lithium metatitanate pebble beds for blanket relevant conditions. All these experiments added information to the database on the thermo-mechanical behaviour of pebble beds, improving our capability to model the HCPB pebble beds under operational conditions.

Acknowledgements

The European Communities within the European Fusion Technology Program supported this work, performed in the framework of the Nuclear Fusion Project of Forschungszentrum Karlsruhe. The authors wish to thank Dr C. Adelhelm for performing the chemical analyses of the ceramics and the staff of the Hot Cells of Forschungszentrum Karlsruhe for the optical microscopy analyses.

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