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Journal of Nuclear Materials 329–333 (2004) 1260–1265
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Post-irradiation examinations of Li_4SiO_4 pebbles irradiated in the EXOTIC-8 experiment

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Abstract

In the EXOTIC-8 irradiation experiment in the High Flux Reactor (HFR) in Petten, lithium orthosilicate (OSi) pebbles with 50% ^{6}Li-content were irradiated with the aim at investigating the behaviour of breeder ceramics at DEMO relevant burn-up. Specifically, changes in the mechanical stability as well as in the tritium release properties (in-pile and out-of-pile) had to be studied. After the completion of the irradiation, lithium orthosilicate pebble samples were shipped to the Research Centre of Karlsruhe (FZK) for post-irradiation examinations. The pebbles irradiated up to about 11% ^{6}Li burn-up showed an increase in smaller cracks in the bulk and the presence of larger through-cracks, but the amount of fragments is quite small and the pebbles maintained a very good crush load. On the basis of these results, it can be concluded that the OSi pebbles can withstand high burn-up irradiation without an unduly high fragmentation.

1. Introduction

For the Helium Cooled Pebble Bed Blanket, which is one of the two reference concepts studied within the European Fusion Technology Program, lithium orthosilicate (OSi) and lithium metatitanate, both in form of pebbles, are the candidate breeder materials. In order to study the behaviour of the ceramics under irradiation at DEMO relevant Li-burn-ups, the EXOTIC-8 irradiation experiment has been carried out at the High Flux Reactor (HFR) Petten, The Netherlands [1]. The main aim was to investigate tritium-release behaviour by in-pile thermal transients and post-irradiation inventory tests and integrity of pebbles after irradiation at DEMO end of life relevant burn-ups. Lithium orthosilicate pebbles were irradiated together with beryllium pebbles in tetra rigs with four independently controlled parallel irradiation channels. The temperature was controlled by gas-mixture technique and on-line tritium release measurements were carried out.

At the Research Centre of Karlsruhe (FZK), Germany, micro-structure, density, mechanical behaviour, out-of-pile tritium release of the lithium orthosilicate pebbles were investigated. In the paper, the results of the post-irradiation examinations (PIE) are discussed.

2. Samples and irradiation conditions

In EXOTIC-8 two capsules of OSi pebbles produced by Schott Glaswerke GmbH by the melting-spraying method [2] were irradiated. They had 50% and 7.5% ^{6}Li-abundance, respectively. The 50% ^{6}Li-enriched pebbles were used for testing the behaviour of the material at high burn-up (about 10%). In-pile tritium release and residence time at burn-up up to 3% were investigated in the material with natural enrichment (7.5%). In order to

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0022-3115/$ - see front matter
doi:10.1016/j.jnucmat.2004.04.235

separate the thermal from the irradiation effects on the pebbles, a thermal annealing (conditioning) was performed on the pebbles before the irradiation: the pebbles were annealed for 3 weeks at 1000 °C (2 weeks in air and 1 week in He atmosphere). The duration and temperature of the annealing was chosen in order to reach in the pebbles conditions comparable to those at end of life in DEMO [3].

At FZK only the material from capsule E8/8 with 50% ^{6}Li-enriched OSi pebbles were investigated. The capsule, containing two annular beds of lithium orthosilicate pebbles separated by a bed of Be pebbles (Brush-Wellman pebbles with 0.1–0.2 mm diameter produced by rotating electrode process), was irradiated in a TETRA assembly positioned in the peripheral HFR core position during 18 reactor cycles. The inner and outer OSi pebble beds had inner radii of 6 mm and 15 mm and outer radii of 10 and 19 mm, respectively; the height of both beds was 220 mm. The density of both pebble beds was 1.45 g/cm^3. The calculated lithium burn-up was 4.11% for the inner bed and 10.87% for the outer one [4]. Four samples of the E8/8 capsule material have been analysed: E8/8-12 and E8/8-32, both irradiated in the upper part of the capsule, in the outer and inner bed, respectively; E8/8-13 and E8/8-33, irradiated at half the height of the capsule in the outer and inner bed, respectively. During irradiation, the mid-plane position of the pebble beds was near the core central line and the temperature at the location of the monitor sets in the pebble beds varied between 350 and 700 °C. The main results of thermal and fast neutron measurements show fluences ranging from 3.4×10^{24} to 4.6×10^{24} n/m^2 for thermal neutrons and 2.7×10^{25} to 2.9×10^{25} n/m^2 for neutrons with energies above 0.1 MeV.

3. Post-irradiation examinations

3.1. Optical microscopy

The enriched OSi pebbles were produced by melting and spraying a mix of 95% ^{6}Li-enriched Li_2CO_3, Li_4SiO_4 and SiO_2 powders. Their final composition was Li_4SiO_4 + 1.4 wt% SiO_2 and they had diameters in the range 250–630 µm. Before the thermal conditioning, they showed a dendritic solidification structure spreading out over the whole cross-section with a network of interdendritic voids, which were due to the high cooling rate during the production. Spherical freezing shrinkage voids and oblong inter-crystalline cavities were present together with micro-cracks. On the surface the dendritic grains had a size of about 50 µm, whereas, in the bulk the grains were in the average about 100 µm long and 20 µm large. After the thermal conditioning, the dendritic structure disappeared and the amount of generated new pores in the pebbles was significantly larger than usually observed in annealed not enriched material. The result has been explained by considering the behaviour of CO_2 in the bulk of the pebbles as residuals from the production. During the annealing, the CO_2 contained in the bulk diffused in the material and was released when it reached open surfaces. In case of reaching closed pores, it accumulated forming bubbles that, expanding, increased the pore dimensions. In later produced batches, the problem has been solved.

Fig. 1 shows an overview of the annealed pebbles before irradiation and Figs. 2–4 irradiated pebbles from E8/8-13 capsule. The pebbles were irradiated in the outer annular bed and 11% Li-burn-up was reached at about 600 °C irradiation temperature. The changes in their colour was mainly due to the reduction of the impurities

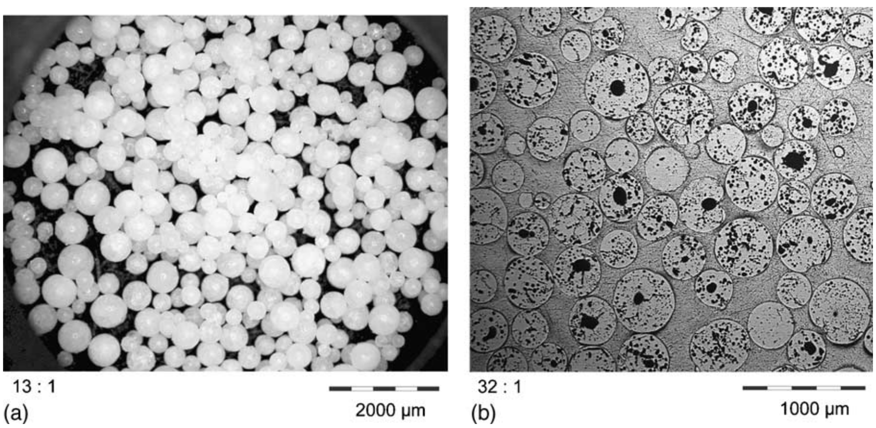

Fig. 1. (a) Overview of annealed pebble OSi before irradiation. (b) Cross-section of annealed OSi pebbles before irradiation (optical microscopy).

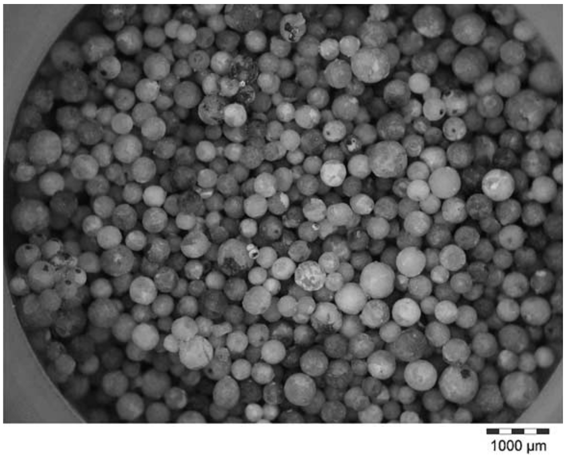

Fig. 2. Overview of irradiated OSi pebbles as delivered at FZK (E8/8-13: outer bed, about 11% burn-up).

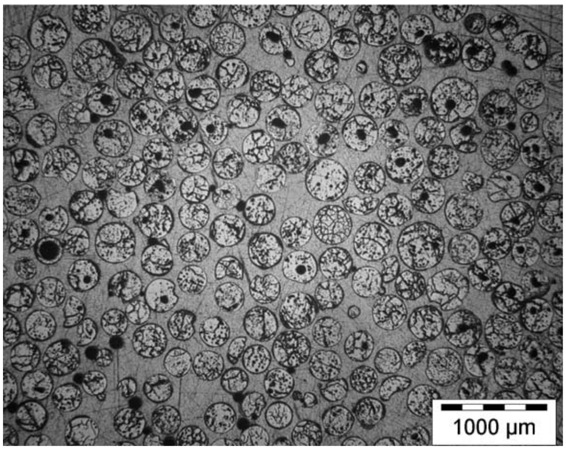

Fig. 3. Overview of the cross-sections of irradiated OSi pebbles (E8/8-13: outer bed, about 11% burn-up).

contained in the pebbles by the purge flow (He + 0.1 vol.% H_2). Some few fragments can be observed among these pebbles, whereas, in some cases, the fragments might be already present in the material before the irradiation. There is a significant increase in smaller cracks in the pebble's bulk and the presence of larger through-cracks. The through-cracks start underneath the pebble surface and open towards the pebble centre. They occur as radial and tangential cracks and in several mixed shapes. The cracks have caused in some cases the fragmentation of the pebbles but the amount of fragments remained quite low. Little new porosity was created during the irradiation. The pebbles irradiated at 4% burn-up (inner bed) were in similar conditions but with lower cracking and a smaller amount of fragments.

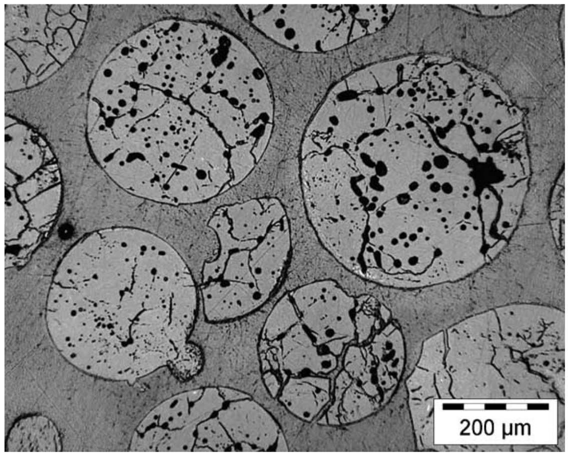

Fig. 4. Cross-section of irradiated OSi pebbles (E8/8-13: outer bed, about 11% burn-up).

3.2. Density measurements and mechanical tests

The density of the pebbles was measured by He-pycnometry (Table 1). This method gives information on closed porosity, which is important because of its possible detrimental effects on tritium release. After irradiation, very slightly reduction in the density has been observed in all batches, i.e. no significant new closed porosity is formed. Globally, i.e. taking into account also the open porosity observed by optical microscopy, a larger reduction in the density of the pebbles might be expected after irradiation.

The mechanical strength of single pebbles was examined by crush load tests, in which a continuously increasing load is imposed onto single pebbles with 0.5 mm diameter, until they break. The pebbles are placed on a glass plate and are pressed by a glass piston in order to avoid any plastic deformation, which could affect the measurements.

Table 1 contains the results of mechanical characterisation. The average crush load of the pebbles after irradiation is comparable with that one of the pebbles in initial conditions (before both annealing and irradiation). This might indicate that the porosity formed during the thermal annealing does not effect significantly the mechanical stability of the pebbles and the decrease in the average crush load measured after thermal annealing might be mainly ascribed to the very strong effect of moisture on the crush load of the pebbles. In fact, the crush loads in initial conditions and after irradiation were measured without drying the material, whereas pebbles after thermal annealing were strongly dried; it has been repeatedly observed in previous tests [3] that moisture can improve the crush load of OSi pebbles produced by melting-spraying method up to

Table 1
Density and crush loads of OSi pebbles (He-pycnometry)

	Osi pebbles before annealing	Annealed OSi pebbles before irradiation	E8/8-12	E8/8-32	E8/8-13	E8/8-33
Density [g/cm^3]	–	2.24 ± 0.006	2.08 ± 0.01	2.12 ± 0.02	2.13 ± 0.01	2.13 ± 0.01
Crush load [N]	8.9 ± 2.6 N	5.66 ± 1.11	7.43 ± 1.02	8.1 ± 1.32	7.23 ± 1.26	8.49 ± 1.29

50%. On the basis of the results, it can be concluded that the irradiated pebbles maintain a crush load comparable with the one of not conditioned/non-irradiated pebbles, in spite of the generated cracking.

3.3. Tritium release

The release rate and total amount of released tritium were studied out-of-pile by heating the irradiated pebbles in a purging flow of He + 1% of H_2. The heating rate was 5 °C/min from 20 °C up to 850 °C, which were held for several hours. Released tritium has been measured using an in-line ionisation chamber. Figs. 5 and 6 show the total tritium release and release rate as function of time and the tritium release rate as a function of temperature for E8/8-13 pebbles. There are two broad main release peaks at about 250 and 600 °C with about 1900 MBq/g of released specific activity. Similar results have been obtained for E8/8-12 OSi, whose released specific activity was about 1200 MBq/g.

The results for the high burn-up capsule are in quite good agreement with those obtained from out-of-pile tritium release measurements of OSi pebbles from EXOTIC-7 irradiation (OSi pebbles with the same composition as in EXOTIC-8, diameters in the range 100–200 μm and burn-up up to about 10%) [5]. The out-of-pile results of both the low burn-up capsule E8/8-32 (51.1 MBq/g) and E8/8-33 (73.5 MBq/g) showed much lower peak release rate, but they had, besides the peak at about 250 °C, another one at temperatures in the range 700–850 °C. For the E8/8-33 the high temperature release rate peak is higher than the one at 250 °C.

Considering the percentage of tritium released during the heating ramp, in relation to the totally released tritium, the batches at higher burn-up (E8/8-12 and E8/8-13) released, at a given temperature, a higher percentage of the contained tritium than the batches at low burn-up. A higher cracking in the pebbles might be the reason for the easier release, which is dominated in lithium orthosilicate by desorption phenomena [6,7].

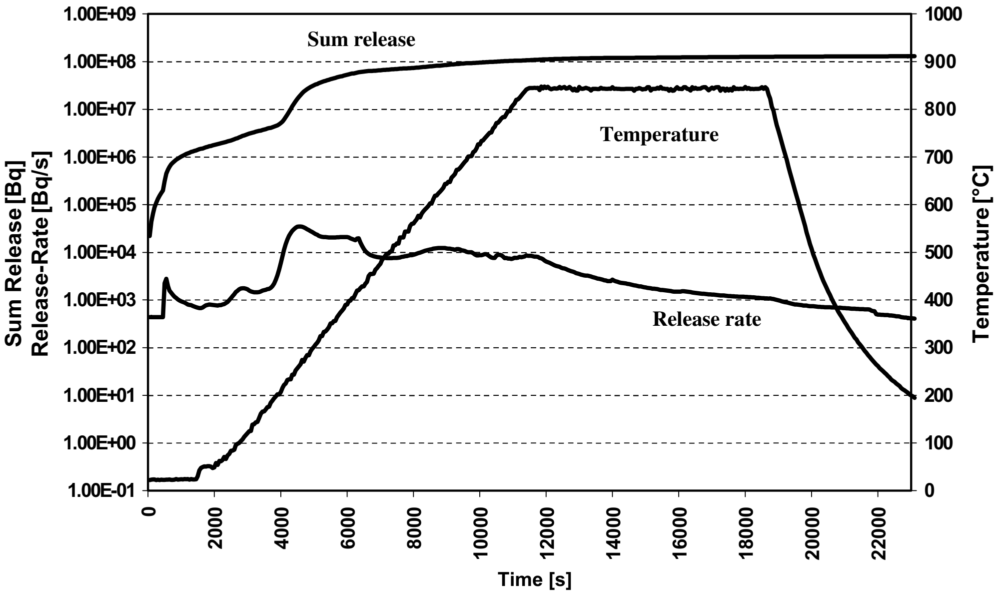

Fig. 5. Sum release and release rate as a function of time (E8/8-13: outer bed, about 11% burn-up).

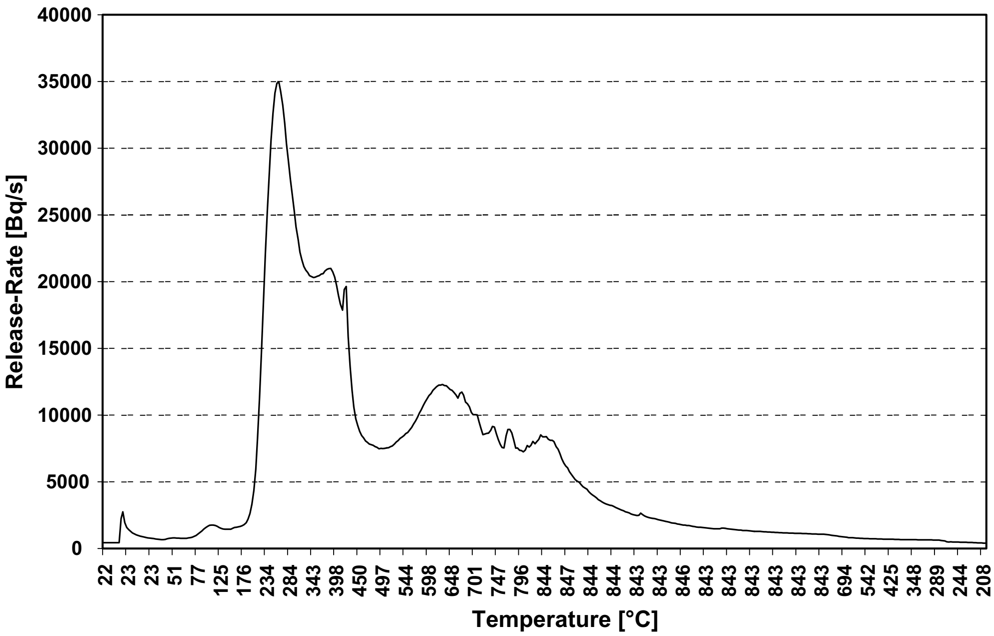

Fig. 6. Release rate as a function of temperature (E8/8-13: outer bed, about 11% burn-up).

The performed out-of-pile experiments are useful for investigating the physical mechanisms of tritium release, but, as clearly observed in Ref. [5], only after considering data from in-pile tritium release and evaluating the tritium residence time, conclusions might be drawn on the in-pile tritium release behaviour of OSi pebbles as a function of temperature.

4. Summary

PIE of Li_4SiO_4 pebbles with 50% ^{6}Li-enrichment have been performed at FZK, after irradiation in the EXOTIC-8 experiment. Before irradiation, the material was thermally conditioned at 1000 °C for 3 weeks and this thermal treatment caused the formation of new large porosity. After irradiation up to about 11% ^{6}Li burn-up, the pebbles show an increase in smaller cracks in the bulk and the presence of larger through-cracks. In some cases, the cracks caused fragmentation of the pebbles. In the material delivered to FZK the amount of fragments is quite small and the pebbles maintained a very good crush load, comparable with the one of not conditioned/not irradiated pebbles. The density of the pebbles, measured by He-pycnometry, showed no significant change, this indicating that no significant new closed porosity was created during the irradiation. Considering both closed and open (observed by optical microscopy) porosity, a decrease of the density might be expected due to the newly formed cracking.

In out-of-pile tests, the pebbles showed peaks of tritium release rate between 250 and 650 °C. In addition, the pebbles with lower burn-up (4%) had also release rate peaks in the range 700 °C–850 °C. Considering the percentage of tritium released during the heating ramp, in relation to the totally released tritium, the batches at higher burn-up (E8/8-12 and E8/8-13) released, at a given temperature, a higher percentage of the contained tritium than the batches at low burn-up. A higher cracking in the pebbles might be the reason for the easier release. A more complete insight can be obtained by considering also in-pile results.

On the basis of the analyses performed on the delivered material, it can be concluded that the OSi pebbles can withstand high burn-up irradiation without an unduly high fragmentation.

Acknowledgements

This work has been performed in the framework of the nuclear Fusion Project of the Forschungszentrum Karlsruhe and is supported by the European Union within the European Fusion Technology Programme.

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