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Thermally induced outdiffusion studies of deuterium in ceramic breeder blanket materials after irradiation

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HIGHLIGHTS

- Surface defects in Lithium-based ceramics are acting as trapping centres for deuterium.
- Ionizing radiation affects the deuterium sorption and desorption processes.
- By extension, the release of the tritium produced in a fusion breeder will be effective.

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ABSTRACT

Based on a KIT–CIEMAT collaboration on the radiation damage effects of light ions sorption/desorption in ceramic breeder materials, candidate materials for the ITER EU TBM were tested for their outgassing behavior as a function of temperature and radiation. Lithium orthosilicate based pebbles with different metatitanate contents and pellets of the individual oxide components were exposed to a deuterium atmosphere at room temperature. Then the thermally induced release of deuterium gas was registered up to 800 °C. This as-received behavior was studied in comparison with that after exposing the deuterium-treated samples to 4 MGy total dose of gamma radiation. The thermal desorption spectra reveal differences in deuterium sorption/desorption behavior depending on the composition and the induced ionizing damage. In these breeder candidates, strong desorption rate at approx. 300 °C takes place, which slightly increases with increasing amount of the titanate second phase. For all studied materials, ionizing radiation induces electronic changes disabling a number of trapping centers for D_2 adsorption.

1. Introduction

Considering the high experimental costs, the long experimental periods and the handling difficulties of activated materials irradiated in fission experimental reactors, the validation of an alternative method for testing the functional properties of tritium breeder materials is an issue.

At Karlsruhe Institute of Technology (KIT) enhanced tritium breeding ceramics are developed for the EU solid breeder concept aiming at modified compositions for the ceramic pebbles to combine the advantages of the two candidate breeding ceramics for ITER, lithium orthosilicate (Li_4SiO_4) and lithium metatitanate (Li_2TiO_3).

In this framework, sorption–desorption experiments of light ion gases in pebble-shaped ceramic materials during ionizing radiation were proposed to simulate DEMO-like ionizing damage and evaluate the material performance under operational conditions to select the best composition among the new KIT candidate pebble materials for ITER experiments. Future approaches will include the modeling of hydrogen isotopes transport in a pebble bed.

2. Experimental part

Lithium orthosilicate-based pebbles, with different metatitanate contents and pellets of the individual oxide components were fabricated by KIT and CIEMAT, respectively.

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Table 1
Material properties of ceramic pebbles.

Li_2TiO_3 content (mol%)	He pycnometry	
	Sample density[a] (g/cm^3)	Close porosity (%)
0	2.383 ± 0.000	0.7 ± 0.0
15	2.458 ± 0.004	3.5 ± 0.2
20	2.467 ± 0.001	5.1 ± 0.1
25	2.455 ± 0.002	7.3 ± 0.1

[a] The sample density measured by He pycnometry does not include the close porosity.

Lithium orthosilicate pebbles with an excess of 2.5 wt.% of silica were fabricated by the established melt-spraying process at SCHOTT AG (Mainz, Germany) [1]. These pebbles with a composition of about 90 mol% lithium orthosilicate (o-LiSi) and 10 mol% lithium metasilicate are the present reference material for ITER. The pebbles exhibit a density of about 95–96% and a very low close porosity of about 1%.

To enhance the mechanical properties, presently lithium orthosilicate pebbles with lithium metatitanate (m-LiTi) as a second phase are fabricated by a modified melt-based process [2,3]. It could be demonstrated that the crush load of the pebbles is indeed increased with increasing m-LiTi content, and it was observed, that also the close porosity is increased [3,4]. This is assumed to be caused by a lower density of the melt, which results in a lower density after solidification and crystallization of the rapidly quenched droplets. The open porosity is not influenced by the m-LiTi content and is in the range of 2–3%. The sample density and close porosity of the used pebbles measured by helium pycnometry are given in Table 1.

Disk-like shaped pellets of the individual components were fabricated by isostatic pressing the calcined powders followed by sintering in air up to 1150 °C/2 h achieving a total porosity of 22–27% with pore sizes <1 μm. Fabrication of the lithium orthosilicate powder is described elsewhere [5], while a commercial lithium titanate powder was used (Alpha Aeasar, >99.9% powder purity).

A steel mesh container was manufactured for the thermally induced desorption (TID) measurements. Samples were first dehydrated at 400 °C/2 h in vacuum and subsequently exposed to a deuterium atmosphere at room temperature inside a pressurized steel capsule (1 mbar) (Fig. 1). After 25 days in contact with the gas, the amount of desorbed D_2 in the pebbles or pellets was followed as a function of temperature up to 800 °C and at 10 K/min temperature rate (TID experiments) using a mass spectrometer (Pfeiffer Smart Test leak detector. Mass selected: 4 amu; Detection limit of 10^{-12} mbar l s^{-1}; Sensitivity better than 5×10^{-12} mbar l s^{-1} which is equivalent to approx. 10^8 D_2 s^{-1}). See Fig. 2 for a TID set up image.

Fig. 1. Pressurized capsule containing the sample load for deuterium sorption experiments under room and gamma-radiation conditions.

Fig. 2. Set up for the D_2 TID experiments. Pebble samples were contained on the self-made steel bag.

Samples of all compositions were placed inside of the pressurized capsule under 1 mbar of deuterium atmosphere (Fig. 1) and gamma-ray irradiated up to a total dose of 4 MGy and a dose rate of 1.8 Gy/s, inside a ^{60}Co (1.2–1.3 MeV) pool facility (CIEMAT, Madrid, Spain). Routine gamma dosimetry was performed using Red Perspex^{TM} 4034 Harwell dosimeters, having accuracies better than 10%. After the required irradiation time (approx. 25 days), the D_2 TID signal was registered at 10 K/min up to 800 °C.

3. Results and discussion

The experiments performed allow the study of a candidate breeder material behavior to D_2 sorption and its subsequent desorption when being stimulated with temperature. The material sorption behavior, either adsorption (adhesion to surface) or absorption (permeation or diffusion into the solid), was compared both outside and inside gamma-ray facility. From results, conclusions on the role of D_2 trapping centers and the defects involved are obtained and therefore will allow inferring the role of the ceramic surface to tritium release during fusion reactor operation.

The desorption behavior of two pebble samples (o-LiSi and o-LiSi + 25% m-LiTi) before and after being exposed to gamma-ray irradiation is plotted in Fig. 3. The temperature behavior of an as-received composition is also included in the plot. The very low D_2 desorption signal of the as-received pebbles for the whole temperature range has then been considered as noise. The most remarkable fact when comparing these curves is their similarity: the thermally induced gas release behavior is comparable although the material is being irradiated during D_2 absorption. Two main desorption processes can be highlighted: the low temperature, shown as a singular peak centered at approx. 300 °C, and the high temperature, represented by a continuous gas release. The high temperature process indicates the continuous release of trapped gas in deep centers or its prior diffusion from absorbing centers, which requires high activation energies. On the other hand, the low temperature peak could be due to gas desorption of adsorbed D_2 in radiation-induced oxygen-related defects at the material surface, as observed in the literature by means of other techniques [6]. But the presence of the same desorption peaks in the unirradiated samples suggests that the centers active for both sorption processes are intrinsic defects or impurities already present in the as-received condition. Lithium vacancies, F^+, Ti^{3+}… could be potential centers for ionic deuterium to be trapped.

For the two compositions shown in Fig. 3, the D_2 release rate is notably decreased in the irradiated condition, registering a lower gas desorption for both high and low temperature contributions. The mechanisms of D_2 desorption in pebbles seem to be highly

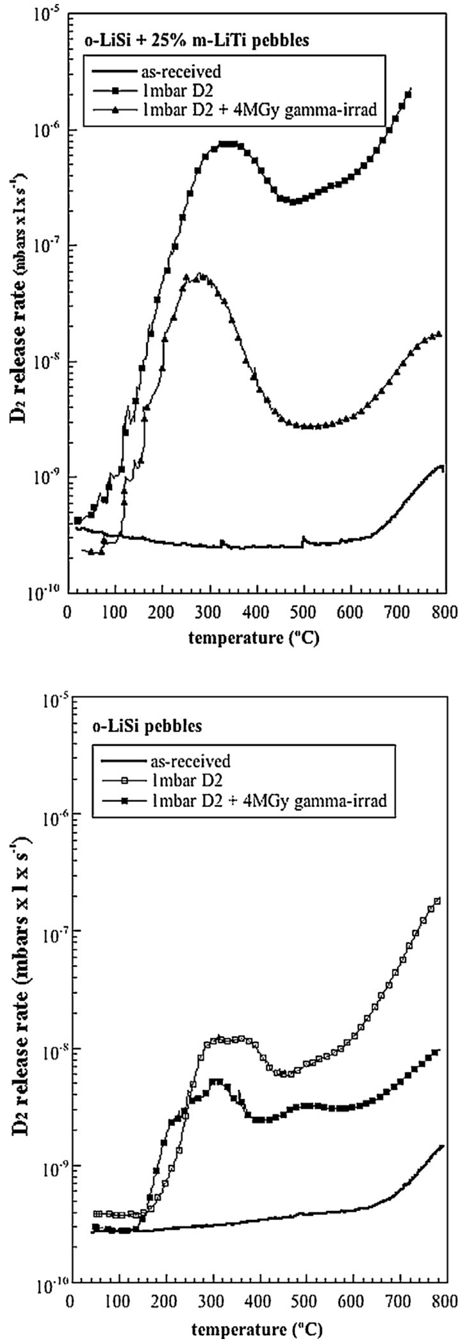

Fig. 3. TID comparative plots of two unirradiated and irradiated samples exposed to 1 mbar D_2 pressure for 25 days.

dependent on the radiation-induced phenomena. During gamma irradiation, secondary electrons are excited and may travel from their stable sites in the crystalline network to be finally trapped in structural defects or due to the presence of impurities. High radiation doses may also reduce the crystallinity and induce further lattice defects acting as scattering centers and energy barriers. Then, the decrease of D_2 desorption could be explained based on the following statements: (a) while irradiating the studied ceramics with ionizing radiation, the mobility of free charges is reducing the active centers for D_2 trapping and therefore the effective concentration of the sorbed gas; and (b) gamma-irradiation is producing both the ionization of the deuterium gas inside the chamber and the sputtering of surface ions (i.e. O, Li), giving rise to ions association in the gas phase, resulting in the reduction of

Table 2
Activation energies (E_a) corresponding to TID processes at low (<300 °C) temperature.

m-LiTi content (mol%)	E_a-LT process (eV ± 0.01)	
	Unirradiated	Irradiated
0	0.19	0.12
15	–	0.13
20	0.20	0.15
25	0.17	0.13

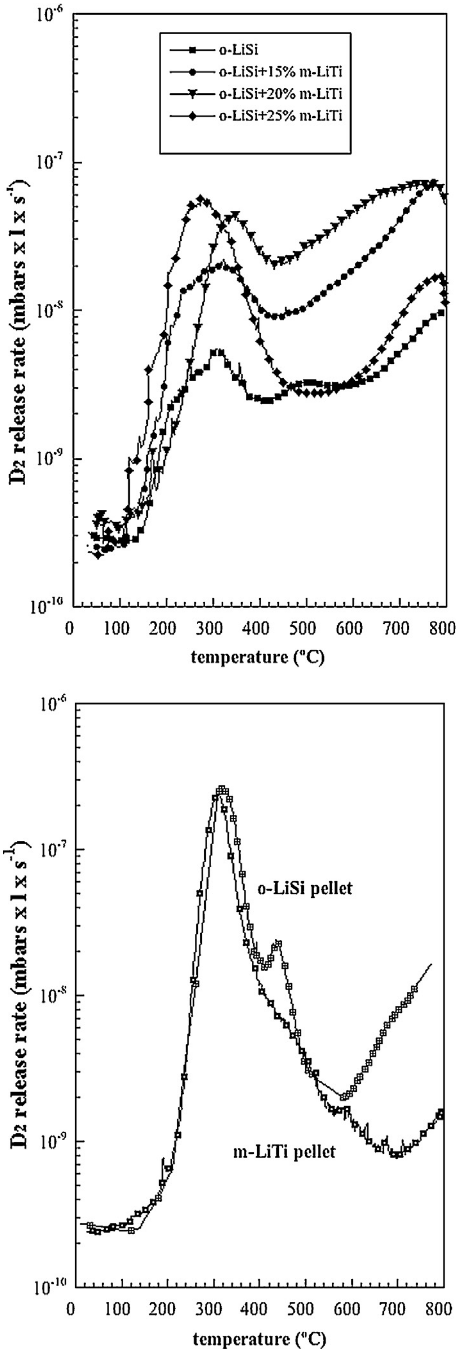

Fig. 4. TID curves of pebble- (upper plot) and pellet-shaped (lower plot) compositions exposed to a 1 mbar D_2 gas pressure during a total dose of 4 MGy gamma radiation.

the effective amount of deuterium to be sorbed and trapped. Further experiments are now in progress to evaluate the sorbed gas fraction and therefore to what extent the last possibility could be considered.

The activation energies (E_a) of the low thermal desorption process for the as received and irradiated samples are calculated and the experimental values listed in Table 2 as a function of the m-LiTi content. Energy data are calculated from the slope of the desorption curves using the initial temperature points (below 300 °C) since a unique process is assumed to contribute. Taking into account this consideration, the high temperature (>600 °C) curve end will require a deconvolution process prior to the accurate calculation of the activation energies for the continuous succession of processes enclosed under the curve. The calculated E_a data point out that: (a) the introduction of variable amounts of the metatitanate second phase does not modify the low temperature desorption mechanism, and (b) gas sorption while irradiation slightly enhanced the desorption dynamics. These partial results are suggesting that the presence of the titanate phase and the ionizing radiation does not provide new or different trapping centers, the trapping centers involved in the orthosilicate sample desorption process being those occurring in the mixed pebbles.

Deuterium desorption curves of all compositions studied after 4 MGy gamma-ray irradiation are plotted comparatively in Fig. 4. The increase of the D_2 release rate at 300 °C with increasing amount of the metatitanate phase is the most relevant feature. Since no new desorption processes are registered when adding metatitanate to the orthosilicate, it should be concluded that the trapping centers are related and common to orthosilicate and metatitanate. Comparing plots on Fig. 4, desorption curves of pellet and pebble-shaped ceramic samples are quite similar. Desorption in pellet samples exhibits the same thermally induced processes, the D_2 release rate being enhanced by a factor of 3 with respect to pebbles. As expected, the highest total (open + close) porosity of pellets results in a great release rate at low temperatures. The increase of the close porosity fraction when increasing the amount of metatitanate in silicate-based pebbles (Table 1) could be then used to justify the greater overall contribution of desorbed D_2. This fact would involve the gas diffusion through the polycrystalline ceramic microstructure prior to its absorption and desorption at close pores, a complex mechanism that might be observed at temperatures over 500–600 °C (Fig. 4). Although this is a reasonable explanation for surface adsorption processes, further experiments should be conducted to establish whether the crystalline structure influences those processes at higher temperature. This statement is supported by recent experimental results of electrical conductivity [personal communication] and diffusion [7] on D_2 implanted pellets. The mobility of ionic species is enhanced in m-LiTi rather that in o-LiSi due to its layered structure, which favors the diffusive processes involving intrinsic and radiation-induced defects. In-depth profiles of remaining D_2 obtained using the Resonant Nuclear Reaction Analysis at variable annealing temperatures show the fast D_2 migration through the ceramic, but the blocking effect of surface. Trapping sites at ceramic surface were causing the blockage of gas desorption although the amount of released D2 was very small at temperatures as low as 200 °C [7].

4. Conclusions

The mechanisms of D_2 sorption and desorption of lithium ceramic candidates for fusion breeder blankets were analyzed in a simulated fusion operational environment. From the desorption curves and calculated activation energies, the following statements can be inferred:

(a) A low temperature process of low activation energy occurs below 300 °C suggesting that surface defects are acting as trapping centers for D_2. D_2 is also trapped in deeper centers being released at temperatures above 600 °C.
(b) Ionizing radiation up to 4 MGy modifies the electronic structure of defects affecting the sorption and desorption processes.
(c) The trapping centers involved in both processes are common to lithium orthosilicate and metatitanate crystalline structures, although the presence of this second phase increases the number of active centers for D_2 sorption.
(d) For fusion applications, the desorption of deuterium, and by extension also the release of the tritium produced in the breeder at operational temperatures, will be effective for lithium orthosilicate ceramic pebbles, the more efficiency being found for the composition including 25 mol% of a reinforced lithium metatitanate second phase.

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