Journal of Nuclear Materials 489 (2017) 229–235

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Tritium adsorption/release behaviour of advanced EU breeder pebbles

Matthias H.H. Kolb*, Rolf Rolli, Regina Knitter

Institute for Applied Materials, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany

A R T I C L E I N F O

Article history:
Received 21 July 2016
Received in revised form
23 March 2017
Accepted 27 March 2017
Available online 6 April 2017

A B S T R A C T

The tritium loading of current grades of advanced ceramic breeder pebbles with three different lithium orthosilicate (LOS)/lithium metatitanate (LMT) compositions (20–30 mol% LMT in LOS) and pebbles of EU reference material, was performed in a consistent way. The temperature dependent release of the introduced tritium was subsequently investigated by temperature programmed desorption (TPD) experiments to gain insight into the desorption characteristics. The obtained TPD data was decomposed into individual release mechanisms according to well-established desorption kinetics.

The analysis showed that the pebble composition of the tested samples does not severely change the release behaviour. Yet, an increased content of lithium metatitanate leads to additional desorption peaks at medium temperatures. The majority of tritium is released by high temperature release mechanisms of chemisorbed tritium, while the release of physisorbed tritium is marginal in comparison. The results allow valuable projections for the tritium release behaviour in a fusion blanket.

1. Introduction

Advanced ceramic breeder pebbles composed of a mixture of Li_4SiO_4 (LOS) and Li_2TiO_3 (LMT) are fabricated and developed at KIT by a special melt-based process named KALOS [1–3]. The development of these pebbles is carried out in view of a future DEMO reactor. The produced pebbles are easily characterized for their non-nuclear properties. For instance, the increased strength of the material with increased LMT content has been documented by Knitter et al. [4]. In recent publications, the mechanical strength of the pebbles is mostly pictured as the most important property of breeder pebbles. Although this view legitimate when constant operation and safety are concerned, the main task of a tritium breeder material is the generation and release of tritium. Therefore, it is crucial that these characteristics are investigated during the development as well.

As neutron irradiation experiments are expensive and require several years of planning, preparation and post irradiation examination (PIE) in addition to several years of irradiation, the comparably rapid development of the breeder pebbles cannot be supported by classical neutron irradiation experiments. Therefore the out-of-pile loading of the pebbles with tritium is used instead as it can be conducted much more easily and frequently. But it has to be kept in mind that the results of such loading procedures are not entirely comparable with neutron irradiation experiments as the generation of tritium within the bulk material is missing. While the Reference OSi material was included in past neutron irradiation experiments and the tritium release investigated out-of-pile as well as in-pile [5–9], such information is not yet available for the advanced ceramic breeder pebbles.

In the presented work, the loading of current grades of advanced ceramic breeder pebbles with different LOS/LMT compositions as well as pebbles of a current reference lithium orthosilicate batch, produced by Schott AG, Mainz [10], is described. Subsequently, the controlled, temperature dependent release of the introduced tritium is detailed to gain insight into the desorption characteristics. As the pebble size can be an influential parameter on the measurements, this factor is addressed by focusing on monosized pebbles. Temperature programmed desorption (TPD) experiments are an often used way to characterize materials and surfaces, for instance catalysts [11–13]. But also in studies of reference grade tritium breeder ceramics, TPD experiments are widely used to gain insight into the release behaviour of tritium [6,8,9,14–16]. In most cases, these TPD experiments were performed as part of PIE.

In this study, novel advanced ceramic breeder pebbles fabricated by the KALOS process were examined together with one batch of reference OSi pebbles fabricated at Schott AG, Mainz. The obtained experimental data was decomposed into individual

---

* Corresponding author.
E-mail address: matthias.kolb@kit.edu (M.H.H. Kolb).

http://dx.doi.org/10.1016/j.jnucmat.2017.03.051
0022-3115/

release mechanisms according to well-established desorption kinetics by a simulated annealing fitting procedure. Such an attempt was rarely made in the past, as acquired TPD curves were mostly discussed in a qualitative way.

2. Experimental

The KALOS pebbles feature three different nominal compositions of LOS/LMT, i.e. 20 mol% LMT, 25 mol% LMT and 30 mol% LMT. The Reference material consists of 90 mol% LOS and 10 mol% of lithium metasilicate (LMS). To eliminate potential effects of the surface area of the samples, the samples were screened and two pebble sizes, i.e. 560 μm and 630 μm, were selected for the experiments. In total eight individual samples were thus available for the experiments (see Table 1).

As neutron irradiated pebbles are not available, the pebbles were loaded with tritium. The loading process was performed individually on each sample right before the TPD experiment. Special care was taken to keep the timespans between all experimental steps low and constant. Each pebble sample was dried for 1 h in inert gas atmosphere at 300 °C in the first step of the loading process. Then the actual loading was performed in a sealed containment which was flooded with hydrogen gas containing 500 ppm tritium and heated to 850 °C. As a result, a maximum pressure of 4 bar was achieved. After loading the samples at 850 °C for 6 h, the containment was cooled to room temperature at a rate of 3 K/min.

There are many ways to perform TPD experiments. Yet, the use of a temperature ramp during desorption is the most convenient way to carry out such experiments. For the TPD experiments, the loaded samples were placed in a tube furnace which is purged by a constant stream (25 ml/min) of reference purge gas (helium with 0.1% hydrogen). The purge gas stream is led through a zinc bed at 370 °C to reduce any tritiated water into hydrogen isotopologues (see Fig. 1). This step also prevents the adsorption of tritiated water within the system. When the gas passed the zinc bed it is led through a proportional counter, with an internal volume of 150 ml, to detect the desorbed tritium as a function of time. Taking advantage of the, although limited but sufficient, solubility of hydrogen in water, two water bubblers in series are used to catch all released tritium. The vast majority of tritium is caught by the first water bubbler, indicating that all tritium is eventually caught by both bubblers. A precise analysis of the activity of the bubbler water after the completion of a TPD experiment makes it possible to normalize the obtained values of the proportional counter in retrospect. For this analysis a scintillation counter is used. All piping where tritium containing gas is led through is kept at 250 °C to prevent noticeable internal adsorption. Once the samples are in place, the furnace is ramped from room temperature to 1080 °C at a rate of 7.1 K/min, while the sample temperature as well as the released activity is constantly monitored. The time resolution of the proportional counter amounts to 30 s.

Once the maximum temperature is reached, it is kept for 2.5 h to ensure that the tritium leaves the pebbles completely. It was verified by a rerun measurement that the pebbles are fully exhausted from tritium by this temperature program. Before each measurement run, an empty run is performed to be able to remove any background from the apparatus in a later step from the recorded data.

Table 1
Compilation of the used samples.

Sample name	Nominal composition	Pebble diameters	
Reference OSi (OSi)	90 mol% LOS + 10 mol% LMS	560 μm	630 μm
KALOS 20 LMT (K20)	80 mol% LOS + 20 mol% LMT	560 μm	630 μm
KALOS 25 LMT (K25)	75 mol% LOS + 25 mol% LMT	560 μm	630 μm
KALOS 30 LMT (K30)	70 mol% LOS + 30 mol% LMT	560 μm	630 μm

The analysis of the obtained data is performed by applying Bruker-AXS TOPAS v5, which is by design a Rietveld analysis software for X-ray diffraction data. Yet, it is possible to modify the routines of the software in a way that any data in x-y-format is processable and thus its highly efficient least-squares minimization routines are available for the analysis of TPD data. TOPAS also provides the possibility to use custom fitting functions by its own script programming language. For the analysis just the tritium release during the ramp up of the temperature is considered. A maximum of 10 peak functions (see section 3) with independent parameters were considered to model the experiment at first. These functions are convoluted to form the envelope shape of the experimental data. Yet, only the necessary minimum of functions for modelling the experimental data was used in the later stages of the refinement. To ensure that the minimizations reach the global minimum, the refined parameters of the last refinement were randomized after convergence and used as starting parameters for another refinement cycle. After converging the refined parameters were randomized again and so on, while the best solution is saved. This refinement process, which is also referred to as “simulated annealing”, was carried out for at least 10000 iterations to ensure sufficiently precise refined parameters at the global minimum. The quality of a refinement is estimated by the parameter R_{wp}, which is automatically calculated by TOPAS [17]. The higher the quality of the fit, the lower R_{wp} will be. An excellent fit is obtained for values of about 1, while reasonable fits may show values of about 10.

3. Theoretical treatment

Desorption of a gaseous species A from a substrate can usually be described by a simple kinetic term if the removal of the desorbed species is sufficiently fast, which is assumed for all considerations in this report. As described in equation (1), the desorption rate is proportional to the adsorbed concentration of the species A raised to the power of x, which is the reaction order. The proportionality factor k is generally temperature dependent and can be assumed as an Arrhenius term with a pre-exponential factor k_0 and the desorption energy ΔE_{des} (see equation (2)). However, no other dependence of the desorption kinetics is considered in this approach.

$$-\frac{d[A]}{dt} = k[A]^x \tag{1}$$

$$k = k_0 e^{-\frac{\Delta E_{des}}{RT}} \tag{2}$$

For a temperature ramp TPD experiment, the derivative of time can be converted into a derivative of temperature by using the identity of equation (3), with the heating rate β and the starting temperature T_0. The combination of equations (1), (2) and (3) yields the so-called Wigner-Polanyi equation (4) [18]. In equation (4), the generic factor k_0 has been replaced by a vibrational factor ν_x since its unit is s^{-1} for first order desorption kinetics.

$$T(t) = T_0 + \beta t = T_0 + \frac{dT}{dt}t \tag{3}$$

$$-\frac{d[A]}{dT} = \frac{[A]^x \nu_x}{\beta} e^{-\frac{\Delta E_{des}}{RT}} \tag{4}$$

It should be noted, that the Wigner-Polanyi equation consists of two parts. The pre-exponential part represents the available supply