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Investigation of transient processes of tritium release from biphasic lithium ceramics Li_4SiO_4-Li_2TiO_3 at negative neutron flux pulse

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ABSTRACT

Biphasic lithium ceramics based on lithium orthosilicate Li_4SiO_4 and lithium metatitanate Li_2TiO_3 is one of the most promising materials for breeder blankets of future fusion reactors. One of the important issues of biphasic lithium ceramics application in the fusion reactor blanket is to determine the parameters and mechanisms of tritium transfer within and from the ceramics.

This paper continues the analysis of irradiation experiments carried out at the WWR-K reactor (Almaty, Kazakhstan) with a sample of biphasic lithium ceramics Li_4SiO_4-Li_2TiO_3 (pebbles of lithium orthosilicate with 35 mol% lithium metatitanate with diameter 250—1250 μm). The section of the experiment in which the reactor was temporarily shutdown for 1.5 h was investigated in detail. During this period of time the sample temperature rapidly decreased from 665 °C to 100 °C, generation of tritium and helium in the lithium ceramic sample ceased, but the desorption of previously generated gases from the ceramic surface continued. The experiments were carried out by the vacuum extraction method.

The nature of tritium-containing molecules and helium release for that specified time interval was analyzed. The kinetics of tritium release from ceramics in the experiment during reactor shutdown was simulated and the expression for the effective diffusion coefficient $D = 5e\text{-}11(m^2/s)\bullet exp(-20(kJ/mole)/RT)$ was determined. It was suggested that one the most realistic mechanisms for tritium release is the mechanism associated with both diffusion and desorption of tritium from the pebbles surface and release from the open pores of the pebble.

This mode of the experiment made it possible to estimate the parameters of tritium release immediately after irradiation, which imitates the conditions of breeding blanket operation in the fusion reactor.

Introduction

Biphasic lithium ceramics based on lithium orthosilicate Li_4SiO_4 and lithium metatitanate Li_2TiO_3 is one of the most promising materials for breeder blankets of future fusion reactors [1–4]. These compounds exhibit low activation compared to lithium zirconate Li_2ZrO_3 and lithium aluminate $LiAlO_2$ and show satisfying thermomechanical and thermochemical properties [5–8]. Tritium generation in Li_4SiO_4 is higher than in Li_2TiO_3 because of the higher density of lithium atoms, but data on the tritium release for Li_4SiO_4 are very different [9–11]. The concept of a biphasic mixture of Li_2TiO_3 and Li_4SiO_4 was proposed several years ago in order to realize the advantageous complementarity of these materials [12–14].

One of the important issues of biphasic lithium ceramics application in the fusion reactor blanket is to determine the parameters and mechanisms of tritium transfer within and from the ceramics.

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The processes that determine the release of tritium can include various stages: bulk diffusion of tritium atoms when interacting with defects and vacancies in ceramics; tritium release to the boundaries of ceramic grains; diffusion along grain boundaries; desorption, including exchange reactions on the surface; chemical interaction on the ceramics surface, etc.

There are a limited number of studies devoted to the determination the processes of tritium generation and release in biphasic lithium ceramics based on lithium orthosilicate Li_4SiO_4 and lithium metatitanate Li_2TiO_3, which helped to estimate some effective parameters of its diffusion and desorption. Tritium release behavior from biphasic lithium ceramics was studied mainly in post-irradiation experiments. Thus, Zhou et al. demonstrated that tritium release temperature and shape of the TDS-spectra are dependent on the phase ratio Li_4SiO_4/Li_2TiO_3. And in [15] they assessed the effect of neutron dose on the tritium release; it was found that as the neutron fluence was reduced the TDS spectra were shifted toward higher temperatures. In [16] Zhou et al. in post-irradiation TDS experiments found that the tritium generation is enhanced for the biphasic Li_2TiO_3-Li_4SiO_4 comparing to the single-phase Li_2TiO_3. The tritium release kinetics is controlled by the phase ratio of Li_2TiO_3/Li_4SiO_4. In the case of higher Li_2TiO_3 phase ratio, the tritium release is mainly determined by the diffusion process. On the other hand, when the Li_4SiO_4 phase ratio is higher, the tritium release is not only controlled by diffusion and but also influenced by other processes such as de-trapping and recovery of irradiation defects. Yang et al. [17,18] investigated the properties of tritium release from Li_2TiO_3-Li_4SiO_4 and $2Li_2TiO_3$-Li_4SiO_4 ceramic pebbles and it was concluded that the interfaces between Li_2TiO_3 and Li_4SiO_4 can promote the tritium release. In [19] the authors performed a very detailed study of tritium release from biphasic lithium ceramics samples saturated with tritium from the gas phase. Authors of [20] made a comparison of tritium release behavior in Li_2TiO_3 and core–shell Li_2TiO_3-Li_4SiO_4 biphasic ceramic pebbles, which have been irradiated by thermal neutrons in Kyoto University. In post-irradiation T-TDS (Tritium - Thermal Desorption Spectroscopy) experiments of the samples it was observed that for core–shell Li_2TiO_3-Li_4SiO_4 biphasic ceramic pebbles two peaks at lower temperature agree with that of Li_2TiO_3 which can be attributed to tritium release from Li_2TiO_3 including shell and core. The peak at higher temperature is mainly considered as tritium release from Li_4SiO_4.

In the mentioned above studies, reliable data were obtained on the release behavior of tritium from biphasic lithium ceramics, but there remains a need for further clarification of the mechanisms of hydrogen isotopes interaction with these ceramics.

This paper presents the results obtained in a desorption experiment with biphasic lithium ceramics carried out during its irradiation at the WWR-K reactor. The section with a decrease in the reactor power from 6 to 0 MW and a subsequent power increase to 6 MW was analyzed specifically. The Arrhenius parameters of the effective diffusion coefficient of tritium in biphasic lithium ceramics were calculated and an assumption was made about the mechanisms of tritium release from a ceramic sample at the specified time interval.

Materials and method

The test samples of biphasic lithium ceramics pebbles (Fig. 1) containing lithium orthosilicate with 35 mol% of lithium metatitanate (pebble size 250–1250 μm) with the natural ^6Li enrichment were fabricated at KIT (Karlsruhe Institute of Technology) by the KALOS process [12]. A diagram of the pebble manufacturing process and the pebbles size distribution in the pebble bed are shown in Figs. 2 and 3.

The experiments were carried out by the vacuum extraction method. The test samples were irradiated in a continuously evacuated capsule (Fig. 4) in the WWR-K reactor (Almaty, Kazakhstan), and simultaneously the gas composition in the capsule with the samples was monitored. During irradiation, the experimental conditions such as the reactor power level, sample temperature and the residual gases composition in

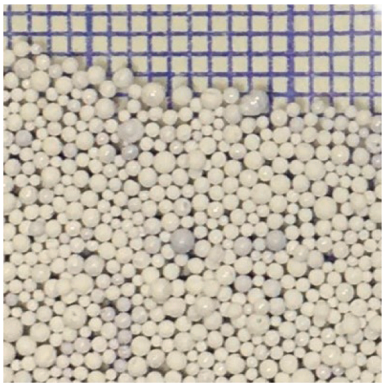

Fig. 1. Appearance of pebbles of Li_4SiO_4-Li_2TiO_3 biphasic ceramics.

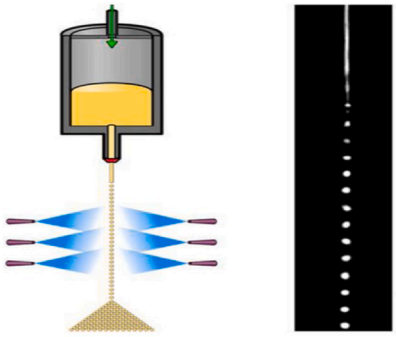

Fig. 2. Schematic of the KALOS process (left), video image of the droplet generation (right) [4].

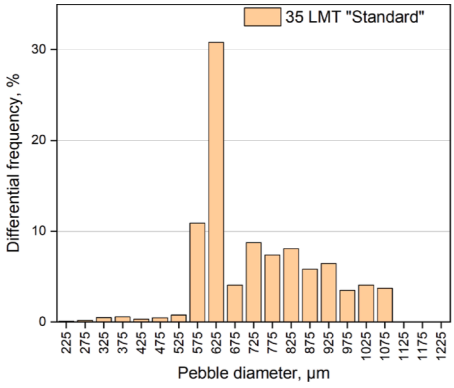

Fig. 3. Pebble size distribution.

the chamber changed. The scheme of the irradiation experiment was presented in detail in [21,22].

In the present work, an analysis of the following section of the irradiation experiment with biphasic lithium ceramics is presented: the moment of reactor short time shutdown and, accordingly, the reduction of the reactor power to 0 MW, irradiation (residual radiation) of the samples at a power of 0 MW, and the moment of the reactor startup up to reach a power of 6 MW.

Some of the experiment parameters are given below:

- Mass of irradiated ceramics – 5.0116 g;
- Irradiation time before the reactor shutdown ~ 3.87 EFPDs (Effective Full Power Day);
- Average temperature of samples during irradiation before the reactor shutdown ~ 665 °C;

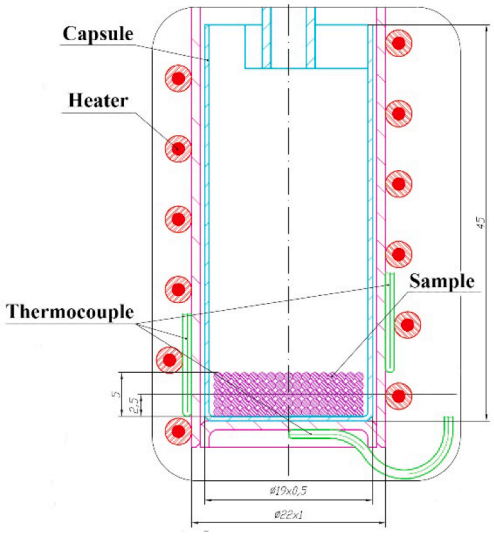

Fig. 4. Irradiation capsule with test samples of biphasic lithium ceramics [21].

- Thermal neutrons flux in the irradiation position ~ $5{\cdot}10^{13}$n/(cm$^2{\cdot}$s);
- Total accumulated thermal neutron fluence up to the reactor shutdown ~ $1.7{\cdot}10^{19}$n/cm^2;
- Reactor shutdown period ~ 1.5 h;
- Average sample heating rate during reactor startup up to reach a power of 6 MW ~ 1.62 °C/s;
- Gas pressure in the chamber with samples ~ $2{\cdot}10^{-6}$ torr.

Results and discussion

Figs. 5 and 6 show a section of the experiment during reactor shutdown for 1.5 h. In particular, the behavior of the residual pressure and temperature in the capsule are given. In Fig. 5 the readings of pressure sensors near turbomolecular pump are shown as P1, and in the area of

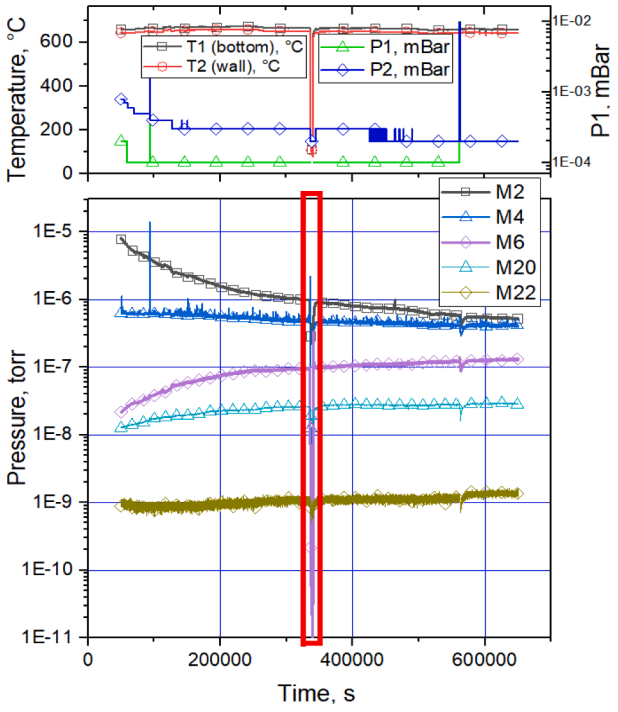

Fig. 5. Full diagram of the experiment, the temporary shutdown of the reactor circled in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

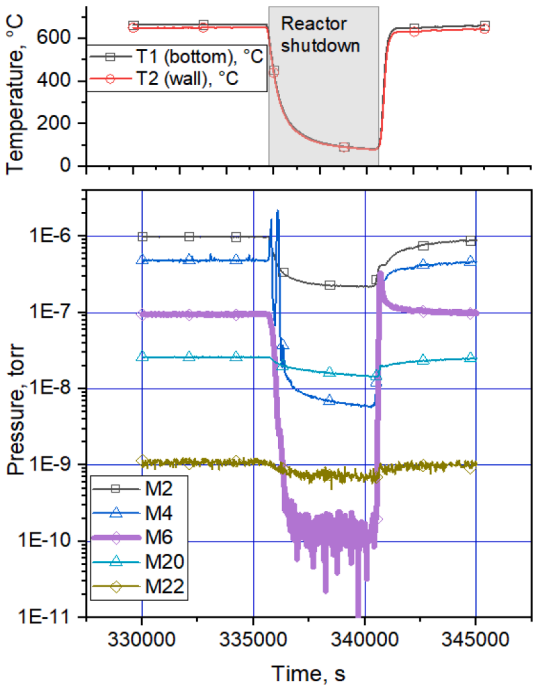

Fig. 6. Gases pressures change in the chamber with samples during a temporary shutdown of the reactor.

the mass spectrometer – P2.

When the reactor was at power, the nature of the gas release from the sample was generally quasi-equilibrium, and in the analyzed section of the experiment, the release of gases with mass numbers M4 and M6 can be considered constant.

During the temporary shutdown of the reactor, a natural decrease in the samples' temperature and the gas pressures in the experimental chamber was observed. Immediately after the start of reactor shutdown process, peak emissions of gases with a mass number M4 were registered. Presumably it was helium only, since no corresponding peaks of T_2 (M6) were observed.

It is worth noting here that this effect was registered in almost all reactor studies performed by the authors earlier: after a decrease in power, usually one or two peaks of helium were observed, which, apparently, are associated with the opening of free paths from the closed pores of ceramics, due to emerging thermal stresses caused by the stop of energy release in ceramics. The release of tritium molecule T_2 quickly drops to zero, while the release of gases He + HT drops by about 30 times and then decreases more monotonically.

When the reactor returns to 6 MW power, a noticeable peak in tritium T_2 release is observed (Fig. 6), which then returns to the values before the reactor's shutdown. It should be noted that during the reactor's shutdown, a significant, about 5 times, drop of hydrogen pressure in the vacuum chamber was registered.

It can also be seen from the Fig. 6 that the pressure of tritium water – M20 and M22, corresponding to HTO and T_2O molecules, are significantly below the values of tritium molecules HT and T_2 pressures. It indicates that tritium water do not significantly affect the balance of tritium release in the irradiation experiment.

The number of tritium atoms released from the samples at the time of the reactor shutdown was calculated as the sum of HT molecules and twice the number of tritium molecules, and presented in the form of transformed curves in Fig. 7.

Simulation of tritium release kinetics

Modeling of the experimental dependences of tritium release from

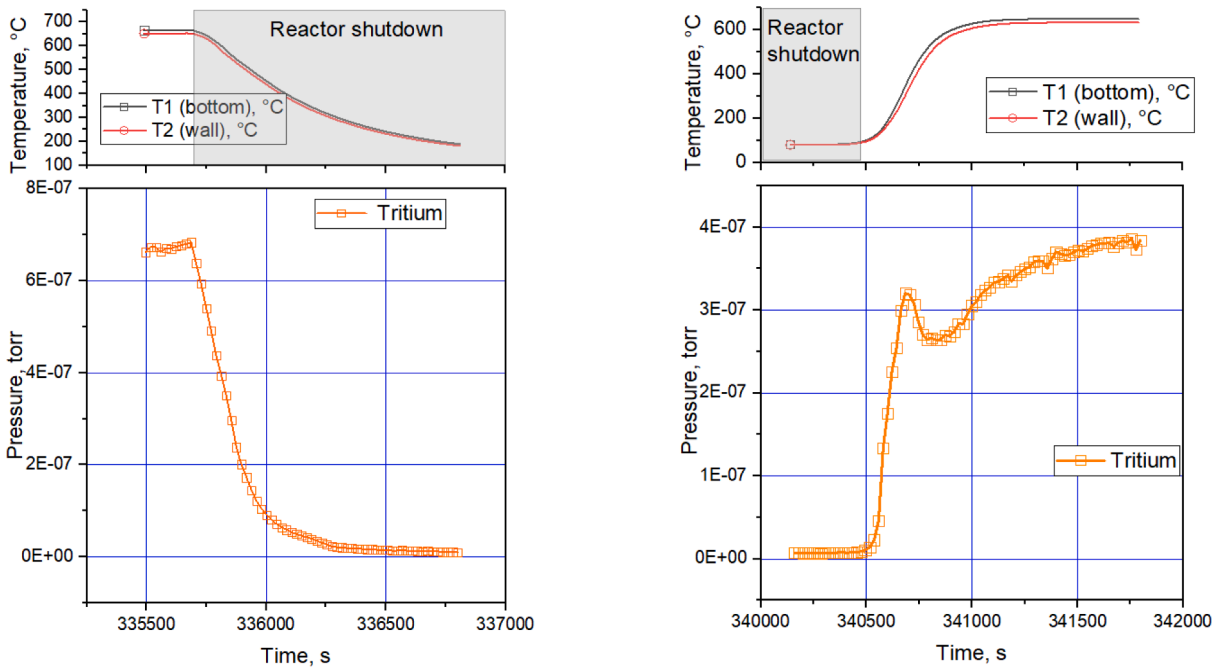

Fig. 7. Total flux of tritium atoms (HT + 2 T_2) from lithium ceramic samples: a) with a decrease in reactor power; b) when the reactor returns to normal power.

lithium ceramic samples was based on the principles of the diffusion-desorption model. It was assumed that these processes determine the rate of tritium release.

Four parameters were varied in the model: the parameters of the Arrhenius dependence of the tritium diffusion coefficient D_0 and E_{dif}, and the desorption rate constants of tritium molecules K_0 and E_{des} corresponding to Eqs. (1) and (2):

$$D = D_0 exp\left(-\frac{E_{dif}}{RT}\right), \quad (1)$$

$$K = K_0 exp\left(-\frac{E_{des}}{RT}\right), \quad (2)$$

where D_0 (m^2/s) is the pre-exponential factor in the Arrhenius dependence of the tritium diffusion coefficient; E_{dif} (kJ/mole) is the diffusion activation energy; K_0 (m^2/(mole•s)) is the pre-exponential factor in the Arrhenius dependence of the tritium desorption rate constant; E_{des} (kJ/mole) is the activation energy of tritium molecules HT and T_2 desorption.

Simultaneous variation of the four parameters of the model will lead to the fact that a large number of sets of these parameters will appear that would satisfactorily describe the experimental curve.

In order to obtain a unique (single) set of these parameters, it was decided to divide the simulation procedure into 2 stages, with the definition of at least 2 parameters at the first stage and 2 parameters at the second stage of simulation. At the first stage, the estimated parameters of the diffusion coefficients were obtained under the assumption that the release of tritium is determined only by diffusion processes in ceramic samples (i.e., diffusion is a limiting process). Changes in tritium concentration in the samples were determined, as well as the tritium flux from them.

The kinetics of tritium release from ceramics in the experiment during reactor shutdown was simulated by the finite element method using the Comsol Multiphysics software.

All pebbles were divided into 5 geometric groups with a characteristic radius, which generally reflected the size distribution of the irradiated pebble bed. It was also assumed during modeling that the samples have an ideal spherical shape and are homogeneous in volume. Here, it should be noted separately that this assumption does not take into account the real structure of the pebble, which has areas of open porosity, but nevertheless allows us to estimate the effective diffusion parameters at a qualitative level.

The distribution of tritium concentration in a spherical sample is determined by the diffusion equation:

$$\frac{\partial C_T}{\partial t} = D\cdot\left(\frac{\partial^2 C_T}{\partial r^2} + \frac{2}{r}\cdot\frac{\partial C_T}{\partial r}\right) + Q, \quad (3)$$

with $C_T(r,0) = f(r)$, $C_T(R,t) = 0$ initial and boundary conditions,

where $r=(0, R)$, R is the pebble radius; $f(r)$ is distribution of tritium concentration over the thickness of the pebble at the initial moment of time, mole/(m^3); C_T is the volume concentration of tritium, mole/(m^3); $\left(\frac{\partial C_T}{\partial r}\right)_{r=R}$ is the tritium concentration gradient on the pebble surface; Q is the source power (tritium generation rate (mole/m^3·s)); D is the diffusion coefficient of tritium, m^2/s.

The mentioned boundary conditions are usually used when describing desorption experiments during vacuum evacuation of a sample, and mean that desorption is not the limiting process in the release of tritium.

In this case, the flow of tritium leaving the pebbles and its time dependence are calculated:

$$F_i = \sqrt{\left(\frac{\partial C_T(R_i)}{\partial x}\right)^2 + \left(\frac{\partial C_T(R_i)}{\partial y}\right)^2 + \left(\frac{\partial C_T(R_i)}{\partial z}\right)^2} \bullet D \bullet S_{surf\,i} \bullet N_i, \quad (4)$$

where $\frac{\partial C_T(R_i)}{\partial x}$ is the gradient of volume concentration of tritium in the pebble boundary; $S_{surf\,i}$ is the pebble surface area with radius R_i, m^2; N_i is the number of pebbles with radius R_i.

A time interval of 20,000 s was chosen as the initial stage of irradiation to calculate the equilibrium distribution of tritium in the samples at the time of the reactor shutdown when the ceramic's temperature was 665 °C (Fig. 8). As initial data in the calculations, experimental data on the reactor power, tritium production rate and sample temperature were introduced.

Thus, using dependences (1)-(3), the parameters D_0 and E_D were

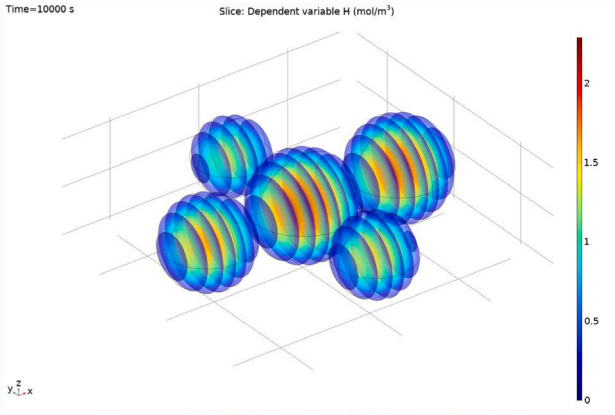

Fig. 8. Distribution of tritium concentration over pebbles of various sizes before a temporary shutdown of the reactor operation.

determined so that the tritium yield curve obtained during the simulation approached the experimental one (Fig. 9). As a result of the simulation, it was also possible to determine the expression for the effective diffusion coefficient, which turned out to be as follows:

$$D = 5e-11\left(\frac{m^2}{s}\right)\bullet\exp\left(-\frac{20\left(\frac{kJ}{mole}\right)}{RT}\right). \tag{5}$$

The obtained values of the diffusion parameters were used as initial estimates for the diffusion-desorption model, which was used further to describe the release of tritium at the second stage of simulation.

Problem (3) was solved with the same initial and modified boundary conditions:

$$C_T(r,0) = f(r), \tag{6}$$

$$\frac{\partial C_T(R_i)}{\partial t} = K(T)\bullet\left(2\bullet {C_{T_{Surf}}}^2 + C_{T_{Surf}}\bullet C_{H_{Surf}}\right) \tag{7}$$

where $C_T(R_i)$ is the volume concentration of tritium, mole/m^3; $C_{T_{Surf}}$ and $C_{H_{Surf}}$ are the concentrations of tritium and hydrogen on the pebble surface.

Here, an additional assumption was used that the rate constants $K(T)$ for the desorption of HT and T_2 molecules from the pebble surface are the same.

The hydrogen concentration was estimated from the ratio of the released fluxes HT and T_2, and Eq. (7) takes the form:

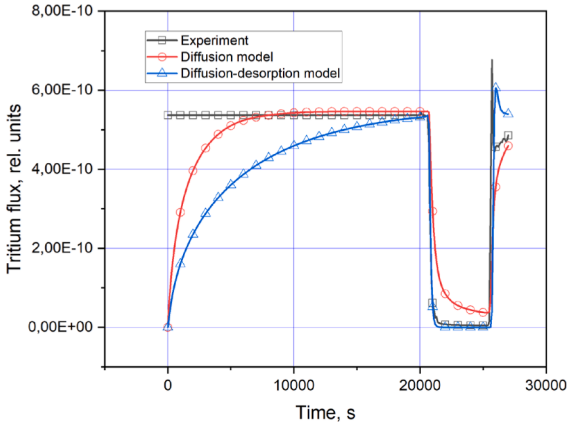

Fig. 9. Modeling the tritium release from the ceramic sample during the reactor shutdown and at nominal power of 6 MW.

$$\frac{\partial C_T(R_i)}{\partial t} = K(T)\bullet {C_{T_{Surf}}}^2(2+\delta(t)), \tag{8}$$

where $\delta = \frac{J_{HT}(t)}{J_{T_2}(t)}$ was defined as the ratio of the HT and T_2 molecules fluxes from the sample. Also, this value was compared and slightly corrected according to the decrease in the curve of hydrogen pressure in the experimental chamber.

As for the tritium concentration on the surface, the authors assumed that it is related to the volume concentration of tritium as follows:

$$C_{T_{Surf}} = \sqrt[3]{C_T(R_i)^2}\bullet 1(mole^{3/2}) \tag{9}$$

Further simulation procedure was similar to that described above, only the tritium flux from the samples was defined as:

$$F_i = K(T)\bullet {C_{T_{Surf}}}^2\bullet(2+\delta(t))\bullet S_{surf\,i}\bullet N_i. \tag{10}$$

The results of the fitting are shown in Fig. 9, and the parameters of the desorption rate constant are shown in the equation:

$$K = 1.2\bullet 10^{-4}\left(\frac{m^2}{mole\bullet s}\right)\bullet\exp\left(-\frac{62\left(\frac{kJ}{mole}\right)}{RT}\right). \tag{11}$$

As expected, the diffusion-desorption model describes well the observed pattern of tritium release. The model curve even has a tritium release peak when the reactor reaches power, but not as "sharp" as in the experiment.

As some hypothesis regarding the possible mechanism of tritium release at a negative reactor power pulse, one should consider the influence of the porous structure of pebbles on the release of tritium. Thus, Kobayashi et al. [23] proposed a model that describes the transport of tritium in pebble with respect to its porous structure. The authors of the presented paper, having experience in conducting reactor experiments with lithium ceramics [24], suppose that it is desirable to use a similar model to describe the release of tritium, since the processes of opening internal pores occur during irradiation of ceramics.

The hypothetical mechanism of the porosity influence on the release of tritium, as applied to the presented experiment, could be as follows. Initially, tritium and helium atoms are formed in lithium under the action of neutrons over the entire volume of a solid media of ceramics according to the reaction:

$$Li^6 + n \rightarrow He^4 + T^3. \tag{12}$$

The term "solid media" here refers to the aggregation of grains in the lithium ceramics without pores.

Real ceramic pebbles have a porous structure and, accordingly, they will inevitably contain both systems of open pores, which, as shown in the Fig. 10, communicate with each other and the external environment,

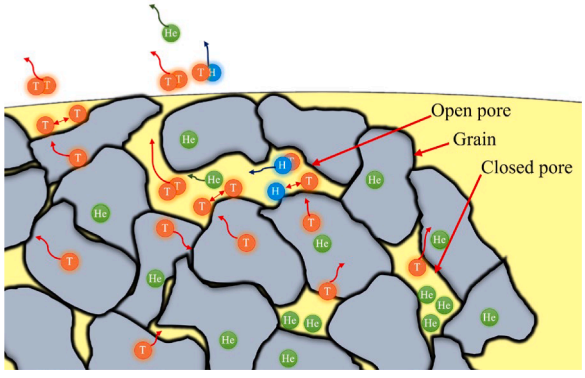

Fig. 10. Mechanism of tritium and helium release from the lithium ceramics pebble.

and closed (isolated) pores.

The release of tritium from a ceramic pebble is the following process. Tritium, formed in ceramics, diffuses in solid regions, reaches the boundaries of open pores or the outer surface of the pebble, after that it is desorbed, forming a T_2 or an HT molecule upon association with a hydrogen atom, and leaves it.

As for the closed pores, tritium, after desorption into the pore volume, is sorbed back on the inner surface of the pore and continues to diffuse in the solid regions of the material until it reaches open pore or pebble surface.

Experiments [24] have shown that the amount of tritium in closed pores is much lower than helium one after one day of irradiation. Thus, tritium formed in ceramics, due to its high diffusion mobility, migrates both through ceramics and through closed pores. The open pores form the so-called "free paths" for the release of tritium.

Such "free paths" will have some resistance, which depends on the cross-sectional size of the pores. In addition, under irradiation conditions, that is, in the presence of thermal stresses and pressures that arise in the pebble bed itself, such "free paths" can change their parameters and even "close", forming closed pores.

In the present experiment, when the irradiation is stopped and the test samples are cooled, due to thermal compression of the pebble material, part of the "free paths" for tritium exit from the pore system closes (their cross-sectional dimensions decrease).

Thus, as the "free paths" close when the pebble is cooled, some of the tritium remains in the closed pores inside the ceramics volume since his mobility decreased at low temperature. After the reactor reaches power and the reverse process of "free paths" opening begins, tritium leaves the pores, forming peaks.

Helium formed as a result of reaction (5) and having an energy of 2.05 MeV thermalizes and enters either the regions of the solid pebble media or pores (if the nuclear reaction proceeds in regions close to the pores). The estimated value of the helium ions path length in biphasic lithium ceramics is about 20 μm. This estimate was made based on the Bethe-Bloch formula [25] using the LISE++ software [26].

Further, it is assumed that a helium atom that enters a solid media does not diffuse in it. And helium, which has moved into the region of open pores or outer surface, leaves the pebble.

The authors suggest that the formation of helium peaks, which was observed in the present experiment at reactor's shutdown and the sharp drop of the sample's temperature, are also associated with the appearance of "free paths" from closed pores to open ones.

Unfortunately, the limited experimental data does not allow any more or less convincing model description of such a mechanism; however, authors suppose that this mechanism can affect the processes of tritium release from lithium ceramics with a change in neutron flux.

Conclusions

In this work, the reactor experiment with 35 LMT lithium ceramics in which the reactor was temporarily shutdown for 1.5 h was presented and analyzed. The samples before reactor shutdown were irradiated in a vacuum environment at a temperature of 665 °C up to the thermal neutron fluence of $\sim 10^{19}$ cm^{-2}.

Within the framework of the diffusion-desorption model, the dependences of tritium release in a given time interval were simulated and the parameters of the Arrhenius dependence of the tritium effective diffusion coefficient in the ceramic sample and the rate constant of tritium desorption from the ceramic surface were obtained were obtained. Data for effective diffusion coefficients of tritium are in a good agreement with the values obtained in [22] for the same ceramics in the initial stage of irradiation experiments. The described mode of conducting experiment made it possible to estimate the parameters of tritium release immediately after irradiation, which imitates the conditions of breeding blanket operation in the fusion reactor.

It was suggested that one of the possible mechanisms for the release of tritium from ceramics is the mechanism associated with both diffusion and desorption of tritium from the surface of pebbles, and with the tritium release from the open pores of the pebble. The post-irradiation experiments with biphasic lithium ceramic samples will be the next stage of research in this direction. The data on tritium yield will be obtained depending on various parameters of the pebbles structure and conditions of irradiation. It is also planned, on the basis of new experimental data and using the approach taking into account pebble porosity [23], to confirm (or refute) the mechanism of tritium release from ceramics proposed in the presented paper, which is associated both with diffusion and desorption of tritium from the pebble surface, and with the release of tritium from the open pores of the pebble.

CRediT authorship contribution statement

Timur Kulsartov: Conceptualization, Writing – original draft, Writing – review & editing. **Asset Shaimerdenov:** Investigation, Writing – review & editing, Project administration. **Zhanna Zaurbekova:** Writing – original draft, Writing – review & editing. **Regina Knitter:** Supervision. **Yevgen Chikhray:** Investigation, Methodology. **Saulet Askerbekov:** Investigation. **Assyl Akhanov:** Investigation. **Inesh Kenzhina:** Formal analysis, Writing – review & editing. **Magzhan Aitkulov:** Investigation. **Darkhan Sairanbayev:** Methodology, Software. **Zhanar Bugubay:** Methodology, Software.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Asset Shaimerdenov reports financial support was provided by Committee of Science of the Ministry of Science and Higher Education of the Republic of Kazakhstan.

Data availability

Data will be made available on request.

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