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Tritium accumulation and release from Li_2TiO_3 during long-term irradiation in the WWR-K reactor

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ABSTRACT

Proposed mathematical and software analysis of reactor experiments allowed interpretation of the experimental results of a tritium release study. Tritium was continuously generated by the reaction of lithium-6 with thermal neutrons for various thermal conditions of lithium metatitanate (Li_2TiO_3). The main gas release parameters were calculated in order to assess the potential use of lithium metatitanate in tritium breeders. These parameters were: gas release rate, tritium retention, retention time, activation energy for thermal desorption as HT, activation energy for volume diffusion as T^+, and the corresponding pre-exponential (frequency) indexes.

1. Introduction

Preliminary experiments of tritium generation and release from lithium ceramics Li_2TiO_3 ($Li_2TiO_3 + 5$ mol%TiO_2) enriched to 96% lithium-6 under long-term (5350 h, 15 campaigns, 2-year experiment) irradiation by thermal neutrons in the WWR-K reactor in Kazakhstan were reported earlier [1]. In that work lithium burn-up was about 23%. Temperature and tritium release were automatically and continuously measured [2]. Characteristics of the samples, apparatus and experimental technique, as well as results of post-radiation studies of changes in physical and mechanical properties of lithium ceramics due to long-term reactor irradiation are given [3,4].

The present paper describes proposed mathematics for the experimental measurement of tritium release processes under reactor irradiation. Main attention is paid to mathematical simulation of release processes of tritium, which is continuously generated in ceramics during stepped heating and cooling of samples. One of the tasks included processing the results of diffusion experiments in order to calculate the diffusion coefficient of tritium in the lithium metatitanate lattice, as well as consideration of possible mechanisms of tritium migration and processes of tritium release during thermal cycling of lithium ceramics in a neutron irradiation field.

2. Mathematical model

The mathematical model proposed in this paper describes the changes in tritium flux under thermocycling the lithium ceramic sample during reactor irradiation.

Experiment showed that the tritium flux depends on temperature – temperature changes (heating or cooling) was accompanied by changes in tritium flux from the sample. A "peak-effect" was observed under the heating mode when the temperature is changed, with an abrupt surge of tritium accumulated at the lower temperature step. The "peak-effect" was not observed for the cooling mode. Data on release of continuously generated tritium during step-by-step heating (alternating stages of heating and cooling) allows solving the inverse diffusion problem and calculating the tritium diffusion coefficient.

The experiment is treated as changes in gas flow from a sphere under stepped changes of sample temperature, both heating and cooling.

2.1. Stepped heating of the ceramic

Degassing of the pebble sample was analyzed in the framework of the classical diffusion mechanism, complying with Fick's law (diffusion) and Henry's law (solubility) taking into account the presence of the sources and sinks under boundary conditions of the first type.

The following factors affecting tritium release were taking into account [5–7]:

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(1) generation of tritium during irradiation (source);
(2) tritium radioactive decay (sink);
(3) tritium depletion of the near-surface layer (layer thickness is the tritium atom recoil distance);
(4) generation of tritiated water due to ion exchange between H_2O and T^+;
(5) possible impact of helium-4 (product of nuclear reaction $^6Li + n \rightarrow {}^3H + {}^4He$ (1)) on the tritium diffusion mechanism: any impact of ^3He (from ^3H decay) was neglected;
(6) molization of atomic tritium to molecular tritium ($2\,{}^3H \rightarrow {}^3H_2$) at open surfaces of a sample.

The role of radiation effects related to irradiation with fast neutrons and gamma-irradiation will be considered in future publications.

Preliminary analysis of these processes showed that the main stage limiting tritium release is bulk diffusion of tritium through the crystal lattice. Thus, the proposed mathematics was based on Fick's second law, taking into account the presence of a continuous source of diffusant evenly distributed through the pebble volume. Solution of the diffusion equation used under boundary conditions of the first type with initial conditions defined by the history of thermal impacts on the sample.

Mathematical simulation was carried out in two steps. At first, time dependence of the tritium flux was calculated for a sphere of r_0 radius under constant temperature. We assumed that at initial moment of time tritium is evenly distributed through a pebble's volume; tritium concentration at the pebble's surface equals zero during all the diffusion annealing. In this case the changes of the tritium concentration prolife are described by the differential equation of Fick's second law:

$$\frac{\partial C(r,t)}{\partial t} = D\left(\frac{\partial^2 C(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial C(r,t)}{\partial t}\right) \tag{1}$$

where $C(r, t)$ – distribution of the concentration of diffusing tritium through the sphere's radius in time t, D – coefficient of tritium diffusion through the lithium ceramic.

Eq. (1) was solved for the initial condition $C(r, 0) = 0$ and the boundary condition $C(r_0, 0) = 0$.

Changes in tritium flux in time were calculated by Fick's first law [8]:

$$J(t) = \left.\frac{\partial C(r,t)}{\partial r}\right|_{r=r_0} \tag{2}$$

Second step included calculation of the changes in tritium flux during stepped changes in the pebble temperature.

Tritium is continuously and evenly generated in the ceramic pebble. The sample is kept at temperature T_1 for time t_1. Then the temperature is sharply increased to T_2 and kept at this level for time t_2, etc. Since the diffusion coefficient changes from D_1 to D_2, the gas flux is sharply increased as well (here $T_1 < T_2$, and $D_1 < D_2$). It is noted that at the new temperature T_2 the tritium flux consists of two components.

First are the "new" molecules, which are born at temperature T_2; their flux is controlled by the diffusion coefficient D_2:

$$J_2(t) = SQ\left[\frac{r_0}{3} - \frac{2r_0}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left\{-\frac{n^2\pi^2 D_2 t}{r_0^2}\right\}\right] \tag{3}$$

where J_2 (atom/s) – complete flux of tritium atoms, generated under temperature T_2, $S = 4\pi r_0^2(\text{cm}^2)$ – square of pebble surface, r_0 (cm) – sphere radius, Q (atm/(cm^3 × s)) – power of source (tritium generation rate).

Second are the "old" *molecules*, which were born at temperature T_1 and were unable to leave during the previous period t_1 (their release rate was controlled by diffusion coefficient D_1), but due to the increase of temperature to T_2 they are able to leave the sphere (the tritium release rate is now controlled by the diffusion coefficient D_2). Flux of these type molecules from the sphere is:

$$J_1(t) = \frac{2\langle C_{(T1)}\rangle S D_2}{r_0}\sum_{n=1}^{\infty}\exp\left\{-\frac{n^2\pi^2 D_2 t}{r_0^2}\right\} \tag{4}$$

Where as a first approximation $\langle C_{T1}\rangle$ (atom/cm^3) is the average concentration of tritium remained in a sphere after sample burnup at temperature T_1 within time t_1:

$$\langle C_{T1}\rangle = \frac{r_0^2 Q}{D_1}\left(\frac{1}{15} - \frac{6}{\pi^4}\sum_{n=1}^{\infty}\frac{1}{n^4}\exp\left\{-\frac{n^2\pi^2 D_1 t_1}{r_0^2}\right\}\right) \tag{5}$$

If the time t_1 during which temperature T_1 is held, is sufficient for establishment of stationary diffusion then

$$\langle C_{T1},\infty\rangle = \frac{r_0^2 Q}{15 D_1} \tag{6}$$

That significantly simplifies the calculations.

Now consider that tritium flux from the sphere at temperature T_2 is described by the equation:

$$\begin{aligned} J(t) &= J_1 + J_2 \\ &= SQ\left[2r_0\frac{D_2}{D_1}\left(\frac{1}{15} - \frac{6}{\pi^4}\sum_{n=1}^{\infty}\frac{1}{n^4}\exp\left\{-\frac{n^2\pi^2 D_1 t_1}{r_0^2}\right\}\right)\right. \\ &\quad \left.\times\sum_{n=1}^{\infty}\exp\left\{-\frac{n^2\pi^2 D_2 t}{r_0^2}\right\} + \left[\frac{r_0}{3} - \frac{2r_0}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left\{-\frac{n^2\pi^2 D_2 t}{r_0^2}\right\}\right]\right] \end{aligned} \tag{7}$$

where D_1 – gas diffusion coefficient at temperature T_1, and D_2 – at temperature T_2.

For long time t_1:

$$\begin{aligned} J(t) = QV\left(1 + \frac{2}{5}\frac{D_2}{D_1}\sum_{n=1}^{\infty}\exp\left\{-\frac{n^2\pi^2 D_2 t}{r_0^2}\right\}\right. \\ \left. - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left\{-\frac{n^2\pi^2 D_2 t}{r_0^2}\right\}\right) \end{aligned} \tag{8}$$

where $V = (4/3)\pi r_0^3$ – volume of spherical granule.

If time t_2 at temperature T_2 is rather large then stationary gas flow is established

$$J = QV \tag{9}$$

Thus, during transfer from temperature T_1 to temperature T_2 we consider that gas flow from sphere is changed from the expression at temperature T_1:

$$J(T_1, t) = SQ\left[\frac{r_0}{3} - \frac{2r_0}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left\{-\frac{n^2\pi^2 D_1 t}{r_0^2}\right\}\right] \tag{10}$$

to the expression at temperature T_2:

$$\begin{aligned} J(t) = QV\left(1 + \frac{2}{5}\frac{D_2}{D_1}\sum_{n=1}^{\infty}\exp\left\{-\frac{n^2\pi^2 D_2 t}{r_0^2}\right\}\right. \\ \left. - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left\{-\frac{n^2\pi^2 D_2 t}{r_0^2}\right\}\right) \end{aligned} \tag{11}$$

Similar formulas describe the behavior of stable gas flow (tritium decay during a reactor experiment can be neglected because of the long half life) during stepped heating to temperatures T_3, T_4, T_5, etc.

Note that the formula describing tritium flow at temperature T_2 does not include the diffusion coefficient directly, but only the ratio D_2/D_1, so it is not possible to determine the values D_1 and D_2 from stepped heating experiments alone.

2.2. Stepped cooling of ceramics sample during irradiation

Now consider the tritium flow under stepped cooling of the sample. Here, $T_1 < T_2$, and $D_1 > D_2$, so the difference in gas retention times is

$$\Delta\tau = \tau_2 - \tau_1 = \frac{\langle C_{T2}\rangle - \langle C_{T1}\rangle}{Q} \tag{12}$$

The mathematical approach is the same as above, but has one significant difference.

If temperature T_1 is rather high and time t_1 is rather long then there will be practically no gas remaining in the sphere, i.e. $\langle C_{T1}\rangle = 0$ and correspondingly $\Delta\tau = \langle C_{T2}\rangle/Q$. Hence, tritium flow at temperature T_2 is changed by the relationship:

$$J_2(t) = SQ\left[\frac{r_0}{3} - \frac{2r_0}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left\{-\frac{n^2\pi^2 D_2 t}{r_0^2}\right\}\right] \tag{13}$$

which allows determination of the diffusion coefficient D_2.

Fig. 1 shows the fitted part of a typical kinetics curve obtained during the experiments for stepped cooling [3]. We see an abrupt reduction of the flow under an abrupt decrease in temperature. Taking account of partial degassing (i.e. presence of tritium in a sample during the higher temperature step) results in a more monotonic dip in the flow in region of the temperature change. However, the dip time is very small and does not have a significant effect on the form of the curve returning to a rise of tritium flux generated at the new temperature step.

Thus, the analysis of the flux dependence with time allows determination of the diffusion coefficient at low temperature under stepped cooling; and for stepped heating – firstly, defining the ratio D_2/D_1, then (using stepped heating curves) calculating the diffusion coefficient at the higher temperature.

3. Discussion

Information obtained as a result of mathematical simulation was used for interpretation of the results of the reactor experiments on tritium release from the neutron-irradiated lithium ceramics.

First of all, the proposed mathematical approach was used for determination of tritium diffusion coefficient in the crystal lattice of lithium titanate by using experimentally measured dependence J(t).

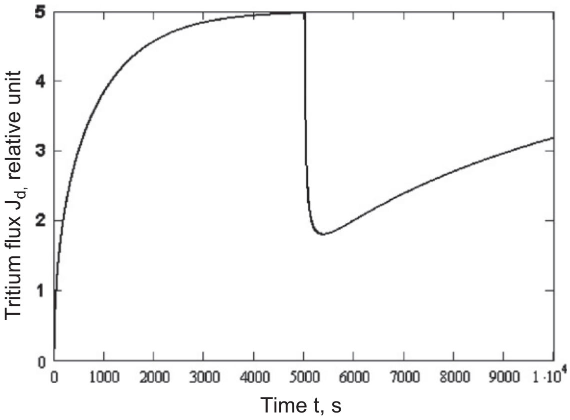

Fig. 1. Release of tritium generated in a sphere taking into account tritium generated during previous temperature steps (stepped cooling).

3.1. Determination of tritium diffusion coefficient in the crystal lattice of lithium titanate

Processing of the experimental data in the framework of the classical diffusion model showed that during the one year irradiation of lithium ceramics in the reactor, the diffusion activation energy was significantly decreased. This is evidence of a decrease of depth of potential wells, along which triton (T^+) diffusion and tritium release in the form of HT and T_2 is realized. The value of the pre-exponential (entropic) factor is decreased as well, that is the evidence of decrease of diffusion paths available for diffusion probably due to creation of radiation defects acting as traps for diffusing tritium.

Analysis of the dependence of flow with time allows determination of the diffusion coefficient at low temperature under stepped cooling; and determination of the ratio D_2/D_1 under stepped heating and then the diffusion coefficient at high temperatures using stepped heating curves. Data on HT and T_2 release (data of stepped cooling from high temperatures, at which degassing of the granules was rather large) were converted to diffusion coefficient of triton (T^+) in the crystal lattice of lithium metatitanate, defined by the stepped heating data.

We assumed that the temperature dependence of tritium bulk diffusion can be described by the Arrhenius law. This dependence of the diffusion coefficient T^+ showed the following values: D_{01} = 0.1 cm^2/s and E_{D1} = 130 kJ/mole during initial lithium burn-up and D_{02} = 0.006 cm^2/s and E_{D2} = 69 kJ/mole during the last parts of the irradiation experiment. Thus, long-term irradiation of lithium ceramics resulted in decrease of activation energy of tritium diffusion by a factor of two and a decrease in the pre-exponential (entropic) factor of diffusion of more than one order of magnitude.

Graphically the temperature dependencies of tritium diffusion coefficient for two stages of tritium burn-up are given in Fig. 2. The same dependencies in Arrhenius scale are given in Fig. 3. Some typical values of the tritium diffusion coefficients in lithium metatitanate for various temperatures and various times are given in Table 1.

For the semiquantitative estimation of diffusion coefficient changes during constant temperature reactor irradiation we used an empirical formula. For example, at 500 °C this dependence to a first approximation can be described by:

$$D(t_r) = 1.59 \times 10^{-10} + 1.28 \times 10^{-7} \times [1 - e^{-0.018\times t_r}] \tag{14}$$

where t_r –irradiation time [9].

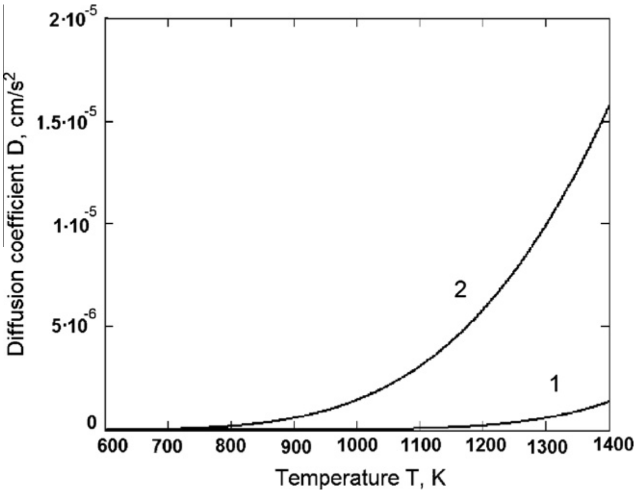

Fig. 2. Temperature dependence of tritium diffusion coefficient by lithium ceramic volume for various stage of 6Li burnup: 1 – initial stage of reactor irradiation, 2 – final stage of reactor irradiation.

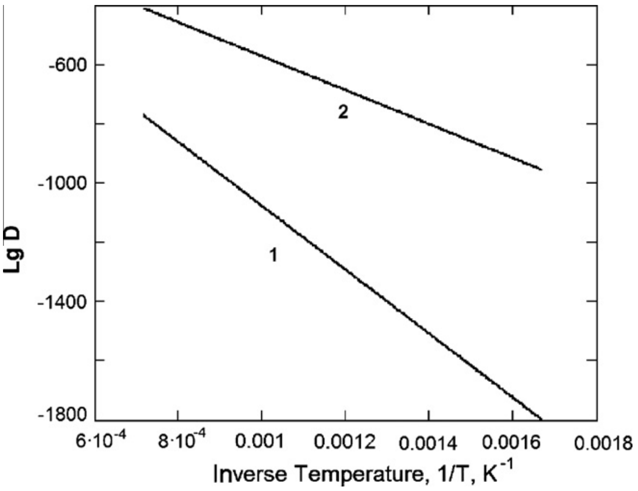

Fig. 3. Data of Fig. 2 Built in Arrhenius coordinates.

Table 1
Diffusion coefficients in lithium metatitanate under various temperatures and times.

Irradiation initial stage		Irradiation final stage	
Temperature, °C	Diffusion coefficient	Temperature, °C	Diffusion coefficient
300	1.35×10^{-13}	300	3.0×10^{-9}
500	1.59×10^{-10}	500	1.28×10^{-7}
700	1.02×10^{-8}	700	1.17×10^{-6}

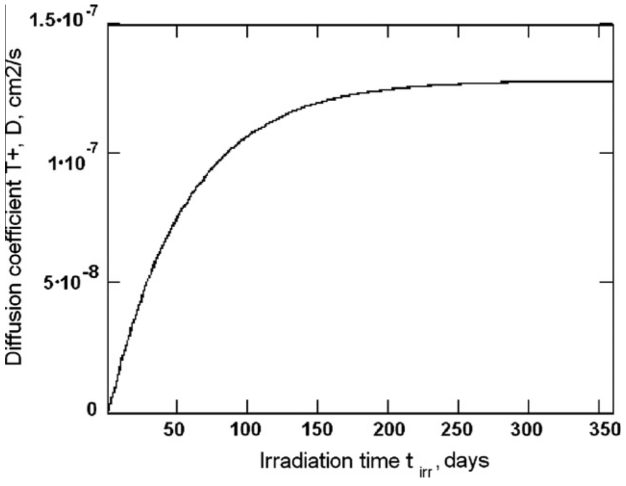

Fig. 4. Example dependence describing change of tritium diffusion coefficient in lithium metatitanate during reactor experiment.

The graph of this function $D(t_r)$ is given in Fig. 4. From this dependence we conclude that the diffusion coefficient increases only during the first 10 months of reactor irradiation, then effectively stabilizes at 1.3×10^{-7} cm^2/s and then does not change significantly. Reaching this limiting value of the diffusion coefficient comes from the balance of two opposing factors – (1) lithium burnup resulting in reduced tritium production and (2) radiation induced defects which trap diffusing tritium. As a result of this balance, the diffusion coefficient doesn't depend on the irradiation duration for the long irradiation times.

3.2. Gas release rate and tritium retention time

When estimating suitability of lithium ceramics as a tritium breeder material, an important parameter is gas release ratio – with values in the range from 0 to 1, where 1 corresponds to stationary flow of tritium from granules.

Table 2
Tritium retention times τ [days], at various temperatures and various stage of lithium-6 burnup in lithium metatitanate.

Temperature, °C	Retention time τ [days], Burnup stage	
	Initial	Final
300	5.7×10^4	2.6
500	48.7	0.06
700	0.76	6.6×10^{-3}

The quantity of $G(t)$ [atom] remaining in the sphere at time t is:

$$G(t) = 4\pi \int_0^{r_0} C(r,t) r^2 dr - \frac{4\pi}{3} r_0^3 C_{(0)} = \frac{8}{\pi} r_0^3 C_{(0)} \left[\frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left\{ -\left(\frac{n\pi}{r_0}\right)^2 Dt \right\} \right] \tag{15}$$

The quantity of gas released from a sphere at time t is:

$$M(t) = \frac{4}{3}\pi r_0^3 C_{(0)} \left[1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2\pi^2 Dt}{r_0^3} \right) \right] \tag{16}$$

And the average concentration of tritium in the sphere is:

$$\langle C \rangle =_{(0)} \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2\pi^2 Dt}{r_0^2} \right) \tag{17}$$

which depends on diffusion coefficient, granule radius and the time period since the beginning of tritium generation in the ceramic [10].

As listed in Table 1, for the initial stage of lithium ceramic irradiation at temperature 700 °C, the tritium diffusion coefficient was 1.02×10^{-8} cm^2/s, and the gas release portion was 13.1% after t = 1 h, whereas for the final stage of the experiment at the same temperature the diffusion coefficient was 1.168×10^{-6} cm^2/s, and gas release portion was 84.4% for the same period. Thus, in our reactor experiments at temperatures higher that 500 °C tritium stationary flow was reached after several hours after the beginning of tritium generation.

Another important criterion is the tritium retention time in ceramics, τ. As known, a retention time τ under constant temperature T depends on gas diffusion coefficient under this temperature, $D(t)$, and size of a sample. The shorter time the generated tritium stays in the ceramic, the better will it be as a breeder material. Retention time was calculated by the formula:

$$\tau(T) = \frac{r_0^2}{15 \cdot D(T) \cdot 3600 \cdot 24} [days] \tag{18}$$

Table 2 includes some calculated retention times.

Table 2 showed that tritium retention times for 1 mm diameter Li_2TiO_3 pebbles range from 57,000 h (in the initial burnup stage) to 10 min (when the burnup of lithium-6 is about 20%). Small retention times under high temperatures make lithium metatitanate-based ceramics a promising breeder material for fusion reactors.

4. Conclusion

It was established that tritium release is mainly controlled by bulk diffusion, however, there is some effect of capture by point defects (trapping) and molization of tritium at the material surface.

Diffusion coefficients and activation energies of tritium release from irradiated ceramics were calculated. When lithium is burned up, the activation energy of tritium release is decreased, tending to a constant value at high burnup levels. The effect is explained by a decrease of lithium ion concentration and the presence of lattice defects acting as additional diffusion barriers. Low retention levels and low retention times lead to low tritium concentrations in pebbles under irradiation at rather moderate temperatures. This allows us to recommend ceramics based on lithium metatitanate as a breeder material for fusion reactors, providing the physical and mechanical properties are conserved during irradiation.

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