STUDIES OF TRITIUM BEHAVIOUR IN NEUTRON IRRADIATED BERYLLIUM PEBBLES FOR FUSION APPLICATIONS

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INTRODUCTION

Increasing energy demands, concerns over climate change and limited supplies of fossil fuels mean that the World needs to find new, ecologically safe and high efficiency energy source. Nuclear fusion of hydrogen isotopes, the process that powers the Sun, is one of the most perspective sources in the future that fulfills the conditions described above.

Fusion reaction of hydrogen isotopes – deuterium $^2$H and tritium $^3$H, is considered to be the most convenient for energy production due to its high energy yield (1).

$^4$H + $^1$H → $^4$He + n + 17.6 MeV 1

Deuterium is the stable isotope of hydrogen that can be extracted from the sea water (its abundance is 0.0156% of all naturally occurring hydrogen). Whereas tritium is radioactive isotope with relatively short half-life (12.3 years) and has to be produced artificially by interaction of neutrons with lithium isotopes, according to reactions (2, 3) in a tritium breeding blanket zone.

$^6$Li + n (thermal) → $^4$He + $^3$H 2

$^7$Li + n (E > 17 MeV) → $^4$He + $^4$He + n 3

Tritium could be produced in reaction of $^6$Li with low energy thermal neutrons, the cross-section of the reaction - 940.4 barns. $^7$Li can also take part in generation of tritium. However, its reaction requires neutrons with higher energy and its cross-section is considerably smaller - 0.3 barns.

To guarantee uninterrupted operation of the reactor it is necessary to ensure complete replacement of the tritium consumed in the D-T fusion reaction, and to decrease neutron losses. Beryllium pebbles are foreseen as a neutron multiplier to the reference concept of the helium-cooled pebble-bed breeding blanket (HCPB) in the European Breeding Blanket Programme for the DEMO design [1]. Neutron multiplying is realized according to the following reaction (4).

$^9$Be + n (≥2 MeV) → $^2$He + 2n 4

Tritium inventory in the beryllium as a result of neutron-induced transmutations (5, 6 and 2) is a significant safety and technological issue for the operation of the breeding blanket.

$^9$Be + n (1-10 MeV) → $^{10}$Be* → $^4$He + 5

$^6$He (0.8 sec) → $^6$Li + β 6

$^6$Li + n (thermal) → $^4$He + $^3$H 2

In the frame of the European Power Plant Conceptual Study, the peak integral gas production in beryllium, at the End-Of-Life of HCPB modules (40 000h operation), has been assessed as 25 700 appm helium and 640 appm tritium, taking account in-pile tritium decay. The global tritium production in the whole of the blanket (390 tons of beryllium) is 23.8 kg [2]. Studies on tritium behaviour in the breeding blanket materials regarding its inventory are of great importance and are performed worldwide.

The scientific organizations in Latvia are also taking part in this research since year 2000 and are coordinated by association AEUL (Association EURATOM – University of Latvia). Laboratory of Radiation Chemistry of Solids of Institute of Chemical Physics is a part of this Association and is involved in studies related to tritium behaviour in neutron irradiated beryllium.

In this paper contribution of association AEUL in the breeding blanket development for fusion application is presented.

Laboratory of Radiation Chemistry of Solids has been involved in the projects related to fusion energy since early eighties when Latvia was still a part of the Soviet Union. At that time research was mainly devoted to the tritium breeder material – lithium containing ceramics, but later also beryllium tiles (plasma facing material) and pebbles (neutron multiplier) were also included. Under the leadership of professor J. Tiliks (1972 - 2007) original equipment was developed that allows studying processes under simultaneous action of a magnetic field, accelerated electron irradiation and temperature. These three are the obligatory factors present in the fusion reactors of a magnetic confinement fusion type (MCF). Therefore it was possible to investigate material behaviour in the conditions relevant to the real reactor operation.

EXPERIMENTAL

SAMPLES

Beryllium samples for these studies have been neutron irradiated in the High Flux Reactor in Petten, The Netherlands. Beryllium pebbles from four irradiation experiments has been studied: BERYLLIUM (1994), EXOTIC 8/3 (2001), PBA (2004) and HIDOBЕ I (2007), whereas for the development of the methods unirradiated beryllium pebbles has been used. Pebbles mentioned above were produced by different manufacturers and methods. Basic
The description of the samples and irradiation conditions are summarized in the Table 1.

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>HIDOBE</th>
<th>PBA</th>
<th>EXOTIC 8/3-13</th>
<th>BERYLLIUM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>NGK Insulators Ltd., Handa City, Japan</td>
<td>NGK Insulators Ltd., Handa City, Japan</td>
<td>Brush Wellman Inc., Cleveland, Ohio, USA</td>
<td>Brush Wellman Inc., Cleveland, Ohio, USA</td>
</tr>
<tr>
<td>Pebble diameter, mm</td>
<td>0.5, 1.0</td>
<td>0.9-1.1</td>
<td>0.1-0.2</td>
<td>Approx. 2</td>
</tr>
<tr>
<td>Irradiation time</td>
<td>646 days</td>
<td>294 days</td>
<td>449.8 days</td>
<td>97.4 days</td>
</tr>
<tr>
<td>Neutron fluence (E&gt;0.1 MeV)</td>
<td>4 - 10 x 10^25 m^-2</td>
<td>3-4 x 10^25 m^-2</td>
<td>2.70 x 10^25 m^-2</td>
<td>1.24 x 10^25 m^-2</td>
</tr>
<tr>
<td>Irradiation temp.</td>
<td>450-700K</td>
<td>420-820 K</td>
<td>800-900 K</td>
<td>780 K</td>
</tr>
<tr>
<td>4He content</td>
<td>3090 appm</td>
<td>300-600 appm</td>
<td>285 appm</td>
<td>480 appm</td>
</tr>
</tbody>
</table>

**TRITIUM CHEMICAL STATE AND SPATIAL DISTRIBUTION**

Technique to distinguish tritium chemical states T₂, T⁰ and T⁻ and to measure its spatial distribution in a metallic beryllium has been developed within these studies and is based on the chemical scavenger and dissolution methods[3].

Pebbles were dissolved in the solutions of

\[
2 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4
\]

and

\[
2 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4 + 0.5 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{Cr}_2\text{O}_7
\]

in a special setup (Figure 1).

Fig. 1 - Schematic view of dissolution system

Following processes are taking place during the dissolution:

\[
\text{Be}^0 + \text{H}^+ \rightarrow \text{Be}^+ + 2\text{H}^0
\]

\[
\text{H}^0 + \text{T}^0 \rightarrow \text{HT} \text{ (gass ph)} \quad K = 1 \times 10^{10} \text{mol}^{-2} \text{atm}^{-1}
\]

\[
\text{T}^0 \text{ (gass ph)} \rightarrow \text{T}^0 \text{ (liquid ph)}
\]

\[
\text{T}^0 \text{ (liquid ph)} \rightarrow \text{HT} \text{ (gass ph)}
\]

One hydrogen molecule corresponds to one beryllium atom and the dissolution rate of beryllium (and hereby also the thickness of dissolved layer for the estimation of tritium bulk distribution) can be calculated from the hydrogen measurements. The rate of hydrogen evolution was measured with a catarometer.

In the solution of molecular and atomic tritium (T₂ and T⁰) of the activities \( A_{T_2} \) and \( A_{T^0} \) respectively, present in a Be sample transfer as T₂+HT into a flow of carrier gas, where the tritium activity released was measured with a gas flow-through proportional meter TEM 2100A with a detector DDH 32.

\[
A_{T} (\text{gass, acid}) = \text{HYPERLINK "http://"}
\]

T⁻ localized in a Be layer remains in the solution. After the Be pebbles had completely dissolved, the tritium activity in the solution, \( A_{T_{\text{sol, acid}}} \), was measured with liquid scintillation method.
In the solution of
\[2 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4 + 0.5 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{Cr}_2\text{O}_7 \]

90% of \(H^0 (T^0)\) reacts with the scavenger \(\text{Na}_2\text{Cr}_2\text{O}_7\) and remains in the solution. Activity of the tritium released into a gas phase and retained in the solution are the respective sums:

\[A_{\text{gas,acid}} = A_{T^0} + x \cdot A_{T^0} \quad (14)\]
\[A_{\text{gas,acid}} = A_{T^0} + (1-x) \cdot A_{T^0} \quad (15)\]

Where value of \(x\) was found experimentally to be 0.1 (10%). Contents of \(T^0, T_2, T'(\text{Bq g}^{-1})\) in a sample were determined separately from the corresponding differences in the activities:

\[A_{T^0} = A_{\text{gas,acid}} - A_{T_2} \quad (16)\]
\[A_{T_2} = A_{\text{gas,acid}} - A_{T^0} \quad (17)\]
\[A_{T^0} = A_{T_2} \quad (18)\]

**TRITIUM THERMO DESORPTION ANALYSIS**

Tritium desorption studies under simultaneous or separate action of temperature, fast electron irradiation and high magnetic field are possible because of the original radiation thermo magnetic setup that has been developed in the laboratory. This equipment is based on the electron accelerator LINAC-4. Schematic view of this original experiment setup is given in a Figure 2.

Sample in a quartz tube is placed in the oven between the poles of the electromagnet. Electromagnet is placed in the front of the electron accelerator. The special hole in the magnet allows electron beam to reach the sample unchanged. The sample is purged with gas mixture of helium + 0.1% hydrogen and the tritium activity in the carrier gas is continuously measured with flow-through proportional meter TEM 2100A with a detector DDH 32. Tritium thermo annealing has been performed at a temperature increase rate of 2.4°C-min\(^{-1}\) and 5.0°C-min\(^{-1}\) up to chosen temperature (280°C-1200°C) and then either stopped heating or held for a chosen time (usually from 1 to 4 h) in a constant temperature.

**STRUCTURE AND CHEMICAL ANALYSIS**

In order to describe and predict tritium behaviour during desorption from neutron irradiated samples, it is necessary to estimate factors that may affect desorption mechanisms. Therefore preliminary examination of the samples has been performed before the tritium release measurements. Such crucial properties as structure and chemical impurities of the samples have been assessed. Structure analysis has been done by the means of the scanning electron microscopy (SEM). Analysis of the chemical impurities in the samples has been performed by several methods, such as X-ray Diffraction, Energy Dispersive X-ray, and Particle Induced X-ray analysis. Analysis of the neutron irradiated beryllium samples is quite complicated due to their gamma activity (even in high purity beryllium there is appm level of \(^{60}\text{Co}\) that transforms into unstable \(^{60}\text{Co}\) as a result of neutron irradiation). This radioactivity leads to significant restrictions on the sample handling. Chemical analysis of the beryllium pebbles is complicate also due to the beryllium transparency to x-rays (EDX and other methods based on detection of the x-rays).

**RESULTS**

Structure of is an essential aspect for the gas migration processes within the solid sample. Significant structure differences has been found if one compares neutron irradiated pebbles produced by IGA and REP methods and irradiated in experiments EXOTIC 8/3 and PBA, respectively (fig.3).

![Diagram](image-url)
Fig. 3 - Beryllium pebbles from PBA (on the left) and EXOTIC 8/3 (on the right) experiments

IGA method gives small, irregular shape pebbles with layered surfaces, whereas REP - large, smooth pebbles with a large void in a central part of pebble. Thermal treatment changes structure of pebbles drastically - it becomes porous and radial cracks are formed (fig.4.).

Fig. 4 - SEM images of PBA pebble after treatment in high temperature (1260°C)

Abundance ratios of tritium chemical forms depend both on the irradiation conditions and properties of the beryllium sample. Comparison of tritium chemical forms in pebbles produced by different methods and irradiated in three different experiments is given in Fig. 5.

Fig. 5 - Abundance ratio of tritium chemical forms in the beryllium pebbles irradiated in experiments BERYLLIUM, EXOTIC 8/3 and PBA

Tritium produced in the neutron induced transmutation of beryllium can diffuse into the lattice or can be trapped by structure traps (such as intragranular He bubbles, closed porosity, grain boundaries, etc.) or it may react with BeO to form \( \text{Be(O)}_2 \) (19) with the formation energy of -0.7eV at the standard temperature, pressure(STP)[4].

Large fraction (up to 96%) of the tritium accumulated in irradiated beryllium pebbles was found to be in the molecular form. We assume that it coexists with the helium in the gas inclusions. Large fraction of gaseous species might be trapped also in the technical void in the bulk of the pebbles that might explain the highest \( T_2 \) content in the pebbles from the PBA experiment (fabricated by the REP method). Presence of molecular tritium in the pebbles is undesirable. In order to extract \( T_2 \) from the metallic matrix it is required \( T_2 \) to dissociate into \( T^0 \) (dissociation energy for hydrogen - 4.52 eV).

In the investigated samples fraction of atomic tritium was in range from 1 – 32%. Atomic tritium can either exist as interstitial or can be trapped in the vacancy–based defect of the beryllium [5]. Atomic tritium can diffuse without any transformation - energy is required only for passing through the diffusion energy barrier. The role of molecular and atomic tritium ratio is obvious if one compares the tritium release from EXOTIC 8/3 and PBA pebbles. From the EXOTIC 8/3 pebbles tritium release is starting at much lower temperatures and full detrition is reached much faster (the diameter difference definitely also has an impact).

Chemically bonded tritium \( T^+ \) was found to be in range from 3-12%. Highest concentration of \( T^+ \) was in the pebbles from the experiment EXOTIC 8/3. According to the chemical analysis these pebbles have the highest beryllium oxide content. Oxide could be formed as a result of the chemical interaction with lithium ceramics during the irradiation (signs of Si were found on the surface of these pebbles). Due to large specific surface oxide content could be increasing also during the storage in air. Tritium retained in the form of beryllium hydroxide stays immobile unless temperature required for dehydration of \( \text{Be(O)}_2 \) is reached (complete dehydration is reached at temperatures above 950°C)[6]. Schematic view of possible tritium accumulation states is showed in Fig. 6.

Fig. 6 - Schematic view of possible tritium states in the neutron irradiated beryllium pebble

To explain the role of tritium chemical forms in tritium desorption process the evolution of chemical forms were studied in the samples irradiated in the EXOTIC 8/3 experiment. Pebbles were heated up to temperatures 280°C and 500°C as long as 15-20% of tritium is released (3 and 1 hour, respectively). Distribution of chemical forms of the remaining tritium in the pebbles was measured (Fig. 7).
Results show that the amount of chemically bonded tritium changes insignificantly after the thermal treatment of pebbles. At low temperature (280°C) only content of atomic tritium has decreased (32% into 16%), other forms had stayed immobile. Heating at higher temperature 500°C decreases the T₂ content due to the molecule dissociation into the mobile T⁰ and also formation of cracks and open porosity where molecular tritium may migrate might be started. Dissociation of molecular tritium is also the reason the atomic form content has increased (16% back into 34%)

Bulk distribution of tritium in the pebbles has been determined for the pebbles of BERYLLIUM and PBA experiments (Fig.8). Distribution was calculated by measuring tritium activity in the gas phase released during the dissolution, therefore distribution of chemically bonded tritium T⁺ was not determined (more likely most of it is in the surface oxide layer and in the oxide inclusions in the bulk). For both types of samples distribution of tritium was similar – low concentration in the first micrometers from the surface, more or less uniform distribution in the bulk and in some pebbles a sharp peak somewhere in the bulk. The peak might indicate the position of the large void that was found during the structure investigations. Whereas low concentration in the first micrometers from surface indicates tritium desorption during storage in the ambient conditions.

Tritium desorption from samples has been studied in order to compare material reliability for fusion applications regarding the detritiation possibility. It was found that tritium desorption from the BERYLLIUM, EXOTIC 8/3 and PBA pebbles starts at different temperatures, moreover these differences reached several hundred degrees Celsius (Fig.9). From the EXOTIC 8/3 pebbles tritium release starts at (90±5) °C (at a temperature increase rate of 5°C/min), whereas from the PBA pebbles release starts at (682±25) °C at a temperature increase rate of 5°C/min and (628 ± 12) °C at the increase rate of 2.4°C/min. From BERYLLIUM pebbles tritium started to release at different temperatures (from 450°C up to 755°C) and it was not possible to determine specific starting point. Typical thermodesorption spectra from each group of irradiated beryllium (BERYLLIUM, EXOTIC 8/3 and PBA) are shown in Fig.9 This significant difference might be caused by several factors; main of them are assumed to be as follows:

- size of the pebble(diffusion length);
- structure (accumulation in the pores, grain boundaries, transportation along the cracks, etc.);
- chemical impurities, oxide content (tritium chemical bonding).
It should be also mentioned that in all thermo desorption spectra separate peaks can be distinguished that might indicate presence of several mechanisms of desorption. Radiation facilitated diffusion and radiolysis in a high magnetic field condition have a significant role in the desorption process of tritium. Therefore, studies of the effect of the fast electron irradiation and high magnetic field on tritium behaviour in beryllium have been performed within this work and detailed analysis done on the beryllium pebbles from EXOTIC 8/3 irradiation experiment. The facilitated release of tritium has been observed as a synergetic effect of irradiation and magnetic field (Fig. 10, Fig. 11)

**DISCUSSION**

Materials used in the fusion devices are exposed to heavy conditions of exploitation. Impact of ionizing radiation and magnetic field has been assessed on tritium containing materials regarding the problem of tritium retention. Tritium accumulation in structural and functional materials is limited to 350 g due to safety reasons. As soon as this limit will be reached reactor will be shut down for detritiation procedure. Many experiments have been performed worldwide for precise estimation of the tritium retention rates and most of the attention has been paid to the plasma facing
materials and tritium breeding blanket materials since they will have either direct contact to tritium containing plasma or tritium will be produced within these materials (tritium breeder materials and neutron multipliers).

In post irradiation/exposure tritium desorption studies performed within this work it has been found that simultaneous action of ionizing radiation and high magnetic field significantly facilitates tritium release - for plasma facing materials (beryllium tiles) even up to factor 7. Whereas up to now in situ measurements of tritium desorption rates under conditions similar to reactor no magnetic field has been used. Therefore it might be concluded that at least for beryllium materials situation in real reactor conditions where high magnetic field is present situation could be more optimistic as it is predicted based on in situ experiments with no magnetic field.

Mechanisms of the facilitating effect of irradiation and magnetic field on tritium desorption from beryllium could be explained by radiation chemistry of gases in the presence of high magnetic field.

As a result of interaction with fast electrons molecular tritium dissociates into atoms. The recombination back to molecule probability is very high, however, at the presence of magnetic field the electron spins of tritium might be changed to parallel and atoms do not react and therefore move away from each other. Atomic tritium further can diffuse through the lattice.

That might be the dominant process responsible for the magnetic field effect in the irradiated beryllium pebbles-beryllium/tritium/helium system.

CONCLUSIONS

(1) Chemical scavenger method and radiation thermo magnetic setup developed in UL Laboratory of Radiation Chemistry of Solids can be successfully applied for studies on tritium behaviour in materials for fusion application.

(2) Simultaneous action of temperature, radiation and magnetic field facilitates tritium release from beryllium pebbles.

(3) Facilitating effect of simultaneous action of temperature, ionizing irradiation and magnetic field is significant and must be taken into account in prediction of tritium behaviour in real reactor conditions.

(4) Detritiation methods based on thermo-annealing of materials could be improved by adding exposure to ionizing radiation and magnetic field.

REFERENCES