UDC 621.039.621.03, 621.039.5.621

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Determination of tritium diffusion coefficients in irradiated beryllium of S-200F grade

Abstract. The work presents study of helium and tritium interaction with irradiated S-200F beryllium grade. The goal of research is related to solving the problem of detritiation of stored beryllium material. Also it is aimed to explain the mechanisms of processes occurring during tritium interaction with beryllium which is planned to be used in the future fusion-type reactor (FTR). The study consists of following stages: thermodesorption experiments on gas release from irradiated beryllium, calculation of helium and tritium generated in beryllium; processing and analysis of experimental data; determination of basic parameters of tritium interaction with irradiated beryllium. These data is needed for estimation of high-temperature degassing procedure such as detritiation method in case of S-200F beryllium grade as well as for calculation of tritium distribution in beryllium materials.
Key words: nuclear, fusion, irradiated beryllium, thermodesorption spectroscopy (TDS), detritiation.

Introduction

One of the main problems for fusion is a choice of the structural materials which are able to carry high thermal and neutron loads at a stationary mode of FTR as well as at a plasma disruption. In ITER beryllium will be used as plasma facing material and as neutron multiplier in certain test blanket's modules. During ITER operation beryllium will be damaged significantly under neutron irradiation. It leads to the generation and accumulation of different radiation defects in beryllium and also helium and tritium nucleus as the products of nuclear reactions on the beryllium atoms.

The full representation of real tritium interaction processes with beryllium is still not clear, moreover there are significant divergences among the determined parameters of hydrogen isotopes with beryllium given by different authors [1–7].

The aim of investigation is to study helium and tritium behavior and determination of effective diffusivities and tritium diffusion activation energy in irradiated beryllium. These data are required for calculation of tritium distribution along the FTR construction, which in turn is necessary for optimization of extraction and disposal of beryllium or tritium future use (for instance, a choice of heating mode for FTR assemblies for the purpose of detritiation).

Objects of research

S-200F beryllium grade was fabricated by Materion Brush Beryllium & Composites Company, USA using vacuum hot pressing technology (HP). Samples were provided for investigation by Japan Atomic Energy Agency (JAEA). The chemical composition of investigated beryllium grade is given in Table 1.

Table 1 – Chemical composition of beryllium

Grade	Mass fraction of impurities, %							
	Be	BeO	C	Fe	Al	Si	Mg	Other metal elements
I-220H	98,6	1,9	0,03	0,06	0,01	0,02	<0,01	<0,04

The samples were irradiated at WWR-K research reactor during 200 hours at temperature of 70° C. The fluencies on fast and thermal neutron were 5,5E+19 cm^{-2} and 9,5E+19 cm^{-2} respectively. Neutron spectrum and neutron flux density are shown in the Figure 1. Sample dimensions and the received dose rates are given in the Table 2.

Samples for TDS-experiments and microstructure studies were made by means of cutting. The each beryllium disk was divided into 4 identical sectors.

Table 2 – Samples' dimensions and dose rates

Be grade	∅, mm	Width, mm	Dose rates, μSv/h
S-200F	9,98 ±0,1	1,51± 0,1	571

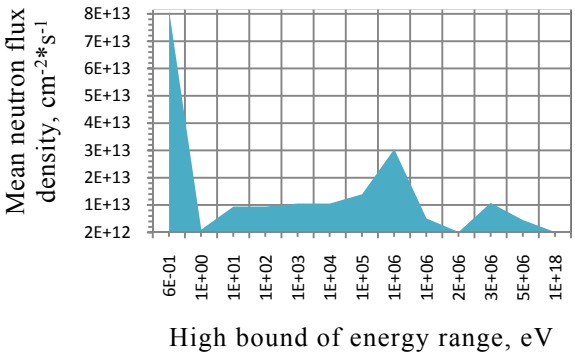
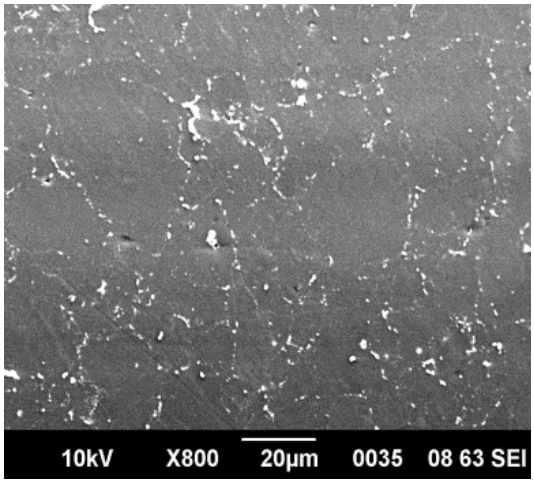


Figure 1 – Dependence of neutron flux density from neutron energy spectrum for VVR-K reactor



S-200F
mean grain size 15 μ

Figure 2 – Results of fine-structural investigation of irradiated beryllium surface

Experimental facility and testing technique

TDS-experiments with irradiated beryllium samples were carried out in Institute of Atomic Energy of National Nuclear Center of Kazakhstan (IAE NNC RK, Kurchatov City) at VIKA facility using methods of thermodesorption spectroscopy in linear heating mode. More detailed description of the facility can be found in work [8].

Results of the microstructure studies

Fine-structural investigation of irradiated samples was carried out before TDS-experiments shown that the microstructures of S-200F beryllium grade is uniform, ordered and similar to each other, there is beryllium oxide on the grain boundary (Fig. 2). These results conform to others literature data for the investigated beryllium grade [9].

Calculation of helium and tritium inventory

Tritium and helium atoms generate in beryllium at the neutron irradiation via following nuclear reactions

1) (*n*, *2n*) at E ≥ 2,7 MeV (580 mbarn)

$$^{9}Be + n_f \rightarrow 2^{4}He + 2n; \quad (1)$$

2) (*n*, α) at E ≥ 0,71 MeV (115 mbarn)

$$^{9}Be + n_f \rightarrow ^{4}He + ^{6}He,$$
$$^{6}He \xrightarrow[T_{1/2} \approx 0{,}85s]{\beta^-} ^{6}Li; \quad (2)$$

Lithium burns almost immediately in thermal neutron flux because of small cross section (945 barn) via reaction

$$^{6}Li + n_{th} \rightarrow ^{4}He + ^{3}H + 4{,}78\ MeV,$$
$$^{3}H \xrightarrow[T_{1/2} \approx 12{,}3y]{\beta^-} ^{3}He. \quad (3)$$

The rest of the reactions don't contribute to the amount of tritium and helium through their small cross section [10].

Taking into account the neutron spectrum and differential cross-sections reactions (1) - it is possible to calculate the amount of gas atoms at the end of irradiation, according to the next two equations followed from expression for neutron reaction rate [11]

$$N_{4He} = 2N(\overline{\sigma_1} + \overline{\sigma_2})\Phi_f, \quad (4)$$

$$N_{^3H} = N\overline{\sigma_2}\Phi_f, \quad (5)$$

where N_{He} – the number of helium atoms;

$N_{^3H}$ – the number of tritium atoms;

$\overline{\sigma_1}$ – the mean effective cross section of reaction (1), cm^2;

$\overline{\sigma_2}$ – the mean effective cross section of reaction (2), cm^2;

Φ_f – the fluence of fast neutron, cm^{-2}.

For the estimation of gas inventory lost from samples' near-surface layer the tritium and helium path lengths were determined using LISE v.9.8.18 program [12]. This program is based on Bethe-Bloch formula for the ionization loss by heavy charged particles with charge *Z* in a medium with *n* electron density

$$-\frac{dE}{dx} = \frac{4\pi n Z^2 e^4}{m_e v^2}\left(ln\frac{2m_e v^2}{\bar{I}^2} - ln(1 - \frac{v^2}{c^2}) - \frac{v^2}{c^2}\right), \quad (6)$$

where m_e – the electron mass; c – the light speed; v – the particle's speed; $\bar{I}$ – average ionic potential of medium substance atoms, trough which particle goes; e – electron charge [13].

The calculated path lengths for tritium and helium in beryllium make 48,2 and 6,9 μ respectively. Besides the counterpart of lost gas from near-surface layer of primary samples was no more than 6% for tritium and 1% for helium.

The period of time was about 4 months from the extraction of sample from reactor until start of TDS-experiments, therefore because of radioactive decay it was lost additionally about 1,8% of tritium inventory, which transformed into ^{3}He.

The determined values of gas inventory in primary beryllium sample are given in Table 3.

Table 3 – The determined values of generated gas inventory

Gas	Gas inventory, ppm
^{4}He	33.08
T_2	1.93
^{3}He	0.04

Results of TDS-experiments and analysis

During TDS-experiments with irradiated beryllium samples the time temperature dependences of gas partial pressure changing were obtained. TDS spectrum for S-200F beryllium grade is shown in the Fig. 3.

According to the TDS-spectra the inventories of T_2 and ^{4}He accumulated in beryllium samples have been calculated. These values have a good matching for investigated beryllium within an accuracy and made 25 ± 3 ppm for ^{4}He and 1,3 ± 0,3 ppm for T_2. How it was guessed the inventory of ^{3}He isotope was slight and made about 0,02 ppm.

Nature of the dependences facilitated to conclude the qualitative features of the helium and

tritium release processes from investigated beryllium:

Helium release mostly in the course of melting processes (1287 ºC) at uniform heating or at temperatures close to the melting point (> 1150 ºC) during significant exposure time (> 1 hour). It happened because of small helium diffusivity in beryllium materials;

Tritium release during melting as well as low-temperature region can be divided into 2 stages:

1) First insignificant detectible peaks of tritium appear at the temperatures of 300—320 ºC and 500 ºC. And at the temperature of 500 ºC helium release also appears at that. The former release (300—320 ºC) is related to the tritium yield from near-surface pores and hollow formations on the surface. The latter release (~ 500 ºC) is caused by multiple cracking and gas yield (helium and also tritium – by formed free venues from hollows and cracks in the sample bulk).

2) In a second temperature range (> 700 ºC) diffusion tritium releases are observed. It should be noted that much more efficient diffusive release is observed for S-200F beryllium grade (Fig.3) than the remaining sorts of investigated beryllium.

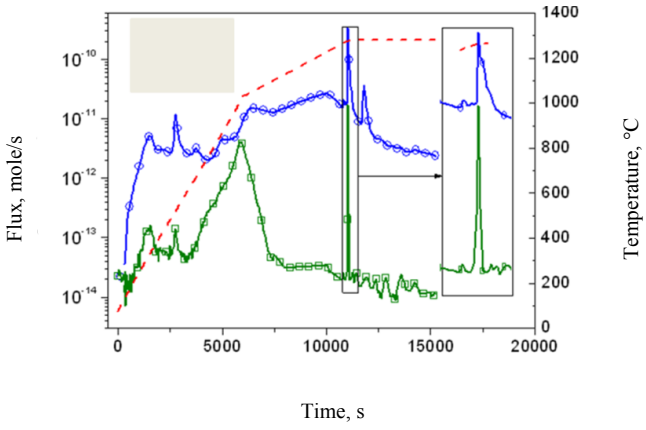


Figure 3 – Time dependence of tritium and helium release from irradiated S-200F beryllium grade (heating rate 40 °C/min): ⊟ — 6Mass; ⊖ — 4Mass

Calculation of the diffusivities

For calculation it has been taken the diffusion model taking into account an irreversible capture of diffusing tritium by a certain trap (helium bubbles, oxygen traps etc.). The presumption about irreversible capture was made on base of the gas release nature from the TDS-spectra: the main gas release is observed at temperatures close to the melting point, consequently it means that particles of tritium and helium are bounded by traps until the melting.

The equations for the diffusion model in presence of the traps

$$\frac{\partial C}{\partial t} = D(t)\frac{\partial^2 C}{\partial x^2} - k_1 C. \qquad (7)$$

The parameters depended on time and temperature are defined additionally

$$D(t) = D_0 \exp\left(-\frac{E_D}{RT}\right),\ k_1(t) = k_{10}\exp\left(-\frac{E_T}{RT}\right),\qquad T = T_0 + \beta t, \qquad (8)$$

where T — temperature of the metal, K; β — heating rate, K/s; t – heating time, s; E_D, E_T — activation energy of diffusion and capture to the traps respectively, kJ/mole; R=*8.31* J/(K·mole) — universal gas constant.

From an initial conditions the concentration of diffusant in the sample is known $C_0(x,\ t = 0)$. For the model approximation the Dirichlet boundary conditions were used satisfied to the conditions of continuous pumping out of diffusant $C(x = 0,\ t) = 0$ и $C(x = l,\ t) = 0$, where l - sample thickness.

Based on this model the simulation of TDS-dependences was implemented. And the parameters of the tritium diffusion in beryllium were determined (Table 3 and Fig. 4).

Table 4 – Parameters of the tritium diffusion in S-65H, I-220H, S-200F beryllium grades

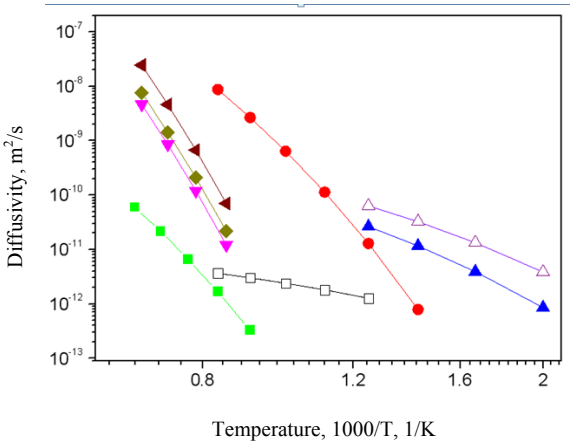
Be grades	The effective diffusion coefficients, D_0, m^2/s	The diffusion activation energy, E_D, kJ/ mole
S-200F	110	280

These values turned out to inflate and mostly matched to the diffusion data for the bubbles of the gas complexes described in the work [5]. The accuracy was defined during the curve-fitting method as maximal deviation of experimental curve from calculated (~20%).

Discussion of the results

Theoretically obtained values of generated gas concentrations in beryllium under irradiation exceed experimentally obtained ones. It is possible that it related to the fact that initial samples were cut mechanically in order to prepare the samples for the experiment. It is suggested that during this procedure the considerable release of gas atoms through radiation defects took place. Moreover, some helium and tritium atoms are left bounded in beryllium even after its melting. Therefore, the experimentally obtained concentrations of helium and tritium in the irradiated beryllium can be considered as reliable.

TDS studies of tritium release from irradiated samples of beryllium lead to the conclusion that moving of gaseous bubbles with tritium in beryllium can be divided into two stages: grain volume diffusion and grain boundary diffusion. However, the grain volume diffusion is a very fast process, and the considerable amount of time is spent to the gas bubbles release to the grain boundaries, which are covered with a film of BeO that is a diffusion barrier.



Literature data: ■ - $D = 10^{-4}\exp(-178{,}6/RT)$ [5];
□ - $D = 3\cdot10^{-11}\exp(-21/RT)$ [4];
● - $D = 4\cdot10^{-3}\exp(-130/RT)$ [6];
△ - $D = 6{,}7\cdot10^{-9}\exp(-31/RT)$,
▲ - $D = 8\cdot10^{-9}\exp(-38/RT)$ [3].
Our data: ▼ - I-220H, $D = 60\exp(-285/RT)$;
◆ - S-65H, $D = 65\exp(-280/RT)$;
▼ - S-200F, $D = 110\exp(-280/RT)$.

Figure 4 – The Arrhenius dependences of the tritium diffusivities in beryllium of various grade defined by different authors

Under high temperatures in beryllium the process of recrystallization is ongoing but it is blocked by the beryllium oxide film on grains. Under temperatures higher than 700 ºC the film of BeO begins to destruct, coagulating into separate inclusions. It allows recrystallization to proceed.

The sample S-200F BeO is distributed by separate inclusions according to Papirov [9], there a lot of dislocations left on the surface while fabricating by HIP. It requires additional energy for annihilation and influences as an additional resistance to the moving of boundaries during recrystallisation. The sample S-200F was made in vacuum and it protected from unnecessary impurities.

It is became clear that as far as grains growth the bubbles of tritium in grains of S-200F beryllium sample are moving actively, yielding to the grain boundaries and then goes to the surface and release. This can explain the effective tritium release by diffusion at temperatures lower than ones of melting.

The mechanism of tritium and helium release mostly depends on the dose of beryllium irradiation if we compare the obtained results with papers [14,15,16] of TDS studies of irradiated beryllium.

In the indicated before papers beryllium was irradiated to higher fluencies (~3E+21, 1E+22 cm^{-2}) than in the present paper (~1E+20 cm^{-2}).

The suggested mechanisms of tritium and helium release was the following: explosive release of helium and tritium from material was observed, which were caused by creation of open porosity as a result of bubbles coalescence and cracking because of high tensions under beryllium swelling.

In the experiments with beryllium irradiated to fluencies higher than 3E+21 cm^{-2} the following effects were observed:

- The considerable decrease of the temperature of tritium release in case of increasing of heating rate (~700 ºC at a heating rate 14 ºC/s, ~400 ºC at a heating rate 90 ºC/s);
- The significant difference between tritium and helium peaks of release.

Therefore, for beryllium irradiated to smaller fluencies, the mechanism of tritium release is less related to the destruction and cracking then to the dissolution of oxide film of BeO at the grain boundaries with the following diffusion of tritium at the boundaries.

Conclusion

The series of TDS experiments were carried out within the study of gas release of irradiated beryllium. The temperature and time dependencies of tritium and helium release from irradiated beryllium were determined.

For samples of the irradiated beryllium the inventories of tritium and helium were calculated theoretically and estimated from experimental data. It can be considered they are in a good agreement in an error order.

The analysis of TDS spectra have shown that for S-200F beryllium grade the main tritium release is concentrated in a diffusion peak.

The microstructure studies of the surface of beryllium samples were carried out before TDS experiments. The data of structure has been obtained.

The mechanism of tritium release is described, taking into account the literature data, data of microstructure analysis and results of TDS experiments.

The processing of spectra of tritium release was carried out using the diffusion model with irreversible capture of tritium by traps. The main parameters of the model and Arrhenius dependencies of effective coefficients of tritium diffusion in the irradiated beryllium were obtained.

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