Modeling of tritium release from beryllium in fusion blanket applications

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Abstract

Only limited data are available on tritium release from irradiated Be. Few models have been suggested for tritium release from beryllium. Simple diffusion/desorption models have been proposed, but lack the capability of accounting for important phenomena such as burst release through interconnected porosity and the effect of the BeO impurity layer.

This paper describes the application of a new model for tritium release from Be, BETTY, to the analysis of recent experimental data. The model includes diffusion through Be and BeO, surface desorption and diffusion through interconnected porosity (as-fabricated or irradiation-induced). Tritium diffusion and desorption coefficients for Be and BeO are estimated from the analysis and compared to previously estimated values.

1. Introduction

Beryllium is considered as both a neutron multiplier material and a plasma-facing component material for fusion reactors. Only limited data [1–3] are available on tritium release from irradiated Be. The data show that most of the tritium generated is retained in the bulk at low temperature. For high density Be samples, a burst-type release is observed at higher temperatures. Few models have been suggested for tritium release from Be. Simple diffusion/desorption models [2,4] which are available for pure diffusion, pure desorption and diffusion/desorption have been proposed, but lack the capability of accounting for important phenomena, such as the effects of the BeO layer and of irradiation-induced helium bubbles.

In order to better understand the tritium transport mechanisms in Be, a more detailed model for tritium release from Be was developed and applied to the experimental data. The model would provide a tool for the analysis of overall tritium behavior in experiments on tritium release from Be as well as in blanket applications. The analysis would help to determine key property data and to focus future experimental activities.

This paper briefly describes the proposed model. A strategy for the analysis of experimental data is then discussed. Based on the analysis, diffusion and desorption coefficients for tritium in Be and BeO are estimated and compared to values obtained from previous experiments.

2. Proposed model: BETTY

Analysis of the Be tritium release results with simple analytical models indicates that tritium release from Be is not controlled by only one simple mechanism, but by a combination of several mechanisms including surface processes. Since the presence of He bubbles after irradiation, as-fabricated porosity and BeO impurity could significantly affect the migration of tritium, they should be included in any comprehensive model. Such a model is proposed here. It is called BETTY (Beryllium Tritium Transport Analysis code), and it includes the following transport mechanisms: (1) production of tritium in the Be and BeO (if present) region, (2) diffusion of tritium in Be/BeO to the interface, (3) second-order desorption at the solid/gas interface, and (4) diffusion of tritium compounds along

inter-connected porosity and removal by the purge
flow. For simplicity, it was decided not to include
trapping in closed helium bubbles in the initial version
of the model but to add it if necessitated by the
analysis.

The model is based on 1-D diffusion. The effective
lengths of the different regions are estimated based on
the assumed geometry that best fits the conditions. For
high density ($\geq 99\%$) samples under normal release
conditions, a slab geometry for the bulk is used, based
on the area of the sample geometry. For porous sam-
ples, a cylindrical geometry for the bulk is used, based
on the concept of interconnected porosity. For the high
density Be under burst release conditions, a 1-D cylin-
drical geometry for the bulk is also used under the
assumption that all He bubbles inside the bulk are
interconnected. The definition of the length of each
region depends on the sample porosity and He-induced
swelling. A more detailed description of the model can
be found in Ref. [5].

3. Existing property data

Beryllium has a high free energy of formation of the
oxide BeO (0.58 J/kg mol) and will form a thin limiting
oxide surface layer. The BeO layer thickness would
vary depending on the sample and experimental condi-
tions, but would be at least within a few nanometers
range [6-9].

The tritium diffusion coefficient in BeO was esti-
mated as follows for single crystal in the temperature
range, 650-1200°C [10]:

$$D_{BeO}(m^2/s)$$

$$= 1.11 \times 10^{-6} \exp(-219.81(kJ/mol)/RT). \quad (1)$$

In the low-temperature range ($< 650°C$) where most of
the experimental data being analyzed in this paper
were obtained, the tritium diffusion coefficient for
single-crystal BeO has not been evaluated. Only values
for BeO power are available in that temperature range.

Previous estimates of tritium diffusion coefficient in
Be vary over a wide range (e.g. Jones and Gibson [11],
Billone [2]), while estimates of second-order desorption
coefficients were not found in the literature. For that
reason, it was decided to focus the analysis on deriving
estimates of both tritium diffusion and desorption coef-
ficients for Be.

4. Analysis of experimental data

Based on the limited available property data, a
strategy was devised in order to estimate consistent
property data based on a systematic analysis of recent

experimental data described in Refs. [1-3]. Key results
and findings from the analysis are highlighted in this
section. More details can be found in Ref. [5].

4.1. Diffusion and desorption coefficients for Be

Data from all five experimental cases (samples Be
No.1, Be No.2, Be No.3, Be No.4 and Be No.5) [1-3]
were first analyzed based strictly on diffusion in and
second-order desorption from Be. For each anneal,
values of the diffusion and desorption coefficients that
produce the best fit to the data were estimated. Arrhe-
nius expressions of both coefficients were then ob-
tained by the least-square method and used to model
the experimental data again. Reproduction of the ex-
perimental results was quite poor overall indicating
that other tritium transport mechanism(s) would also
play a role in determining the tritium release behavior.
Based on earlier discussion, one such mechanism was
assumed to be diffusion through a BeO layer.

Prior to the analysis of data including the BeO
layer, new estimates of the diffusion and desorption
coefficients in Be are required since the previous Ar-
rhenius expressions would also include the effect of the
BeO layer. It seems reasonable to assume that for the
high density samples, the Be surface in contact with
closed irradiation-induced helium bubbles is free of
oxygen. When burst release occurs due to the joining
of these bubbles, it is assumed here that no BeO is
present on the surface of the newly-formed intercon-
nected porosity during the relatively short burst release
time. The diffusion and desorption coefficients for Be
can then be estimated by reproducing the three burst
release cases for high density Be samples. For these
cases the model also includes diffusion through the
interconnected helium-induced porosity. The resulting
tritium diffusion and desorption coefficients for the Be
are:

$$D_{Be}(T)(m^2/s)$$

$$= 4.56 \times 10^{-7} \exp(-104.6(kJ/mol)/RT), \quad (2)$$

$$K_{r,Be}(T)(m^4/s)$$

$$= 4.94 \times 10^{-28} \exp(-110.7(kJ/mol)/RT). \quad (3)$$

4.2. Analysis of BeO layer

Once the tritium diffusion coefficient in Be has
been estimated (Eq. (2)), cases with a BeO layer can be
analyzed. Three parameters need to be determined: (1)
the thickness of the BeO layer, (2) the tritium diffusion
coefficient in BeO, and (3) the tritium desorption coef-
ficient for BeO.

As mentioned in section 3, the BeO layer thickness
would be at least within a few nm range. The diffusion

coefficient of tritium in single crystal BeO has been measured in the temperature range 650–1200°C, as shown in Eq. (1). The desorption coefficient is unknown.

It seems reasonable to choose the 700°C anneal case for the Be No.5 sample [3] and to reproduce the tritium release data based on the diffusion coefficient of Eq. (1) and to find values of BeO thickness, δ_5, (close to a few nanometers) and of desorption coefficient that result in the best fit. These values were found to be $K_{r,BeO} = 5 \times 10^{-35}$ m^4/s and $\delta_5 = 2.2$ nm.

When analyzing the other annealing cases at lower temperature, it is not clear whether the diffusion equation from Eq. (1) would still apply. Specifying the BeO layer thickness would simplify the analysis since it would reduce the parameters to be determined to the desorption and diffusion coefficients only.

4.3. Determination of BeO layer thickness

The tritium release fractions from two similar high density Be samples (Be No.1 and Be No.2) at the same temperature [1] are different enough to suggest a fundamental difference in tritium transport mechanism. A possible explanation is that this is due to different thicknesses of BeO layers on the two samples.

In order to estimate the thickness of the BeO layer for each sample it is assumed that for the four high density samples, the same fraction of the total measured oxygen content is located at the surface and the rest in the bulk. The thickness of the BeO layer on these samples can then be related to each other as shown in Ref. [5]. Assuming $\delta_5 = 2.2$ nm, then $\delta_1 = 18.2$ nm, $\delta_2 = 15.1$ nm and $\delta_3 = 9.6$ nm.

The porous sample (Be No.4) is modeled based on a cylindrical geometry. Thus, it does not seem consistent to evaluate the BeO layer thickness in this case by
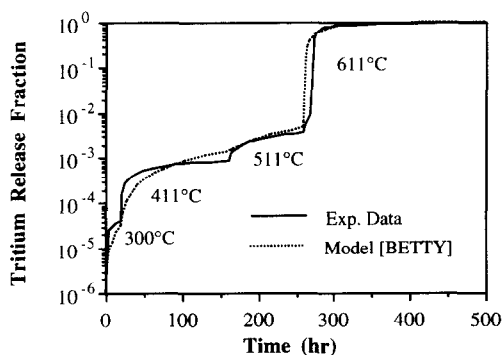

Fig. 1. Comparison of BETTY results with experimental results for tritium release from 100% dense Be under four successive temperature anneals, based on diffusion and desorption coefficients of Eqs. (2), (4) and (5).
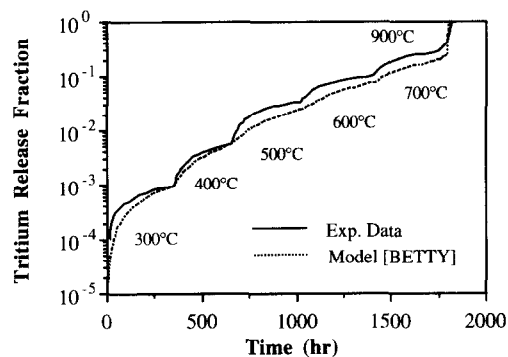

Fig. 2. Comparison of BETTY results with experimental results for tritium release from 99.6% dense Be under several successive temperature anneals, based on diffusion and desorption coefficients of Eqs. (2), (4) and (5).

comparing to the other high density cases. Instead, based on newly determined diffusion and desorption coefficients for BeO, the thickness of the BeO layer for the porous sample can be determined by curve fitting the tritium release results.

4.4. Tritium diffusion and desorption coefficients for BeO

BETTY was used to reproduce the experimental data for the four high-density Be samples under normal release conditions based on the above BeO layer thicknesses. For each temperature anneal, the diffusion and desorption coefficients for the BeO layer, D_{BeO} and $K_{r,BeO}$, that best reproduce the data were determined as a function of temperature in the temperature range $< 650°C$:

$$D_{BeO}(T)(m^2/s)$$

$$= 6.28 \times 10^{-16} \exp(-53.4(kJ/mol)/RT), \quad (4)$$

$$K_{r,BeO}(T)(m^4/s)$$

$$= 1.58 \times 10^{-32} \exp(-57.5(kJ/mol)/RT). \quad (5)$$

Using the diffusion and desorption coefficients of Eqs. (2), (4) and (5), BETTY was applied to the experimental data for porous Be sample (Be No.4), and the thickness of BeO layer which best reproduces the results was found to be $\delta_4 = 18.6$ nm. Figs. 1 and 2 show examples of the comparison of modeling results with the experimental data for sample Be No.1 and Be No.5 using $D_{Be}(T)$ of Eq. (2), $D_{BeO}(T)$ of Eq. (4) ($T < 650°C$) or $D_{BeO}(T)$ of Eq. (1) ($T > 650°C$, Be No.5), $K_{r,BeO}(T)$ of Eq. (5) and $K_{r,Be}(T)$ of Eq. (3) for burst-release cases assuming no BeO.

Overall, the modeling results for the five samples follow the experimental data reasonably well and show much better reproduction of the experimental data

than the results based on diffusion and desorption in Be only. An exception is the Be No.5 sample results which at about 600–700°C is significantly lower than the experimental data. A possible explanation for this is that in analogy to the diffusion coefficient in BeO, the desorption coefficient from BeO at higher temperature might follow a different Arrhenius expression than at low temperature.

5. Comparison of diffusion and desorption coefficients

The Be diffusion coefficient from Eq. (2) was compared to diffusion coefficients of hydrogen isotopes in Be obtained from several release experiments as shown in Fig. 3. The wide range of variation could be explained by the fact that these experiments were performed under a variety of conditions which could cause other transport mechanisms to play a major role such that the estimated different diffusion coefficients obtained are then effective ones. The estimated value of the diffusion coefficient from Eq. (2) tends to be towards the lower end of the range.

The tritium diffusion coefficient for BeO (Eq. (4)) is plotted in Fig. 4 and compared to values from previous experiments. The diffusion coefficient from Eq. (4) at temperatures of 300–600°C is substantially lower from the extrapolated value from the single crystal diffusion coefficient previously measured at higher temperatures. It is much closer to values obtained for BeO powder at similar temperatures. It is conceivable that the diffusion coefficient for single crystal BeO would follow a different function with temperature depending
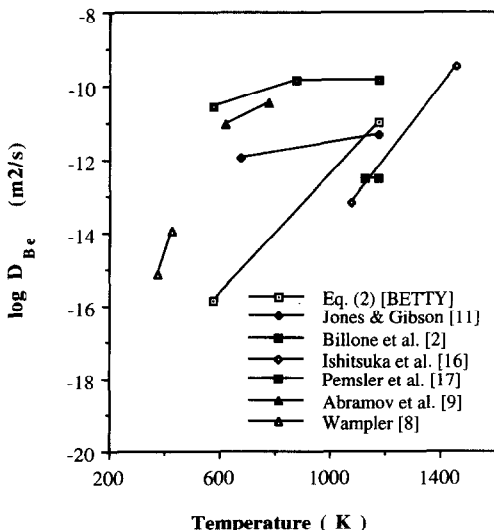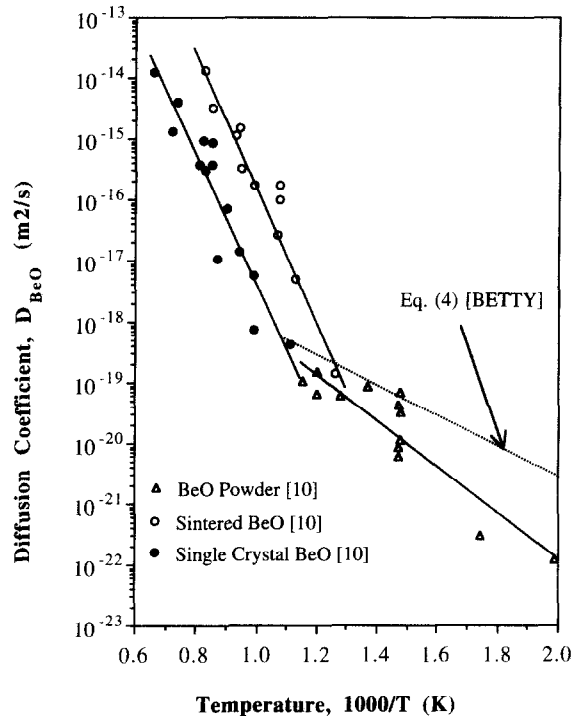

Fig. 4 Comparison of D_{BeO} of Eq. (4) with measured diffusion coefficients for BeO [10]: (1) single-crystal BeO; (2) sintered BeO; (3) BeO powder; and (4) BETTY results.

on the temperature range, i.e. it might follow the single-crystal values previously obtained at temperatures > 650°C and Eq. (4) at temperatures < 650°C.

The desorption coefficients in combination with the diffusion coefficients were compared to other experimentally determined values of $D/2K_r$ for hydrogen isotopes [12–15]. The parameter, $D/2K_r$ referred to as the "pumping parameter", is important to the diffusive and recombinative processes for the hydrogen retention/release in metals and has been determined from experimental data. Based on the tritium diffusion coefficient of Eq. (2) and the desorption coefficient of Eq. (3), the pumping parameter for tritium/Be from this work was estimated and found to be within the range of previous experimental values.

6. Conclusion

Simple existing models were found to poorly reproduce the tritium release data from recent Be experiments, indicating the need for a more comprehensive model. To help understand and interpret the data, a new model, BETTY, was developed, incorporating diffusion in the Be and BeO layer, second order desorp-

Fig. 3. Summary of diffusion coefficient of hydrogen isotopes in Be, based on several experiments and modeling results.

tion, and diffusion through inter-connected porosity and/or irradiation-induced helium bubbles.

In view of the limited property data presently available, a strategy was developed in order to analyze the several types of experimental data for high density and porous Be samples and to estimate diffusion and desorption coefficients for Be and BeO over the experimental temperature range. Based on existing data, diffusion and desorption coefficients for the Be and BeO were estimated by reproducing the release results for high density and porous Be samples.

A comparison of the diffusion and desorption coefficients of tritium in Be with values obtained from previous experiments was performed. Large variations exist in the estimated diffusion coefficient. This might be due to the fact that experiments were performed over a range of conditions which could cause other transport mechanisms or effects such as the presence of BeO layer to play a role. The estimated diffusion coefficients would then be "effective" values.

The tritium diffusion coefficient for BeO estimated here (Eq. (4)) was also compared to the experimental results for single crystal and porous Be samples. This diffusion coefficient at this low temperature ($< 650°C$) is substantially higher than the extrapolated value based on the high temperature ($> 650°C$) single-crystal data. However, it is within the range of values obtained for BeO powder at lower temperatures.

Although the model did reproduce the set of experimental results on tritium release from Be reasonably well, it is still at an early stage and would need to be improved and further validated as additional experimental data become available. Specific areas of improvement include accounting for the effect of trapping in close pores and/or He bubbles and modeling better the kinetics of the BeO surface layer and of the associated surface mechanisms.

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