



Analysis of tritium transport in irradiated beryllium

Seungyon Cho, Mohamed A. Abdou

*Mechanical, Aerospace and Nuclear Engineering Department, University of California, Los Angeles, 43-133 Eng. IV,
Los Angeles, CA 90024-1597, USA*

Abstract

A tritium transport model called BETTY has been developed to describe and predict the kinetics of tritium transport in beryllium in fusion blanket applications. The model incorporates surface processes and trapping in He bubbles, in addition to bulk diffusion. A comparison of the results available for irradiated beryllium samples from the tritium release experiments SIBELIUS with those predicted by the model show reasonable agreement. In addition, a parametric sensitivity analysis for the variation of surface activation energies and diffusion coefficient is performed and the results of the analysis are presented and discussed.

1. Introduction

Tritium transport and release is an important issue for beryllium multiplier in fusion blankets. In order to address this issue, a thorough understanding of the mechanisms of tritium transport is required. Beryllium is a metal to which we can generally apply the concepts of diffusion, solubility, surface processes and traps. Tritium transport in the irradiated beryllium is affected by processes occurring in the bulk, He bubbles and solid–gas surfaces. There are two types of solid–gas surface that have to be addressed in the irradiated beryllium. One is a pure Be–He bubble interface where no oxide layer exists and the other is a bulk (Be–BeO)–purge gas interface. Since the material characteristics of the beryllium and BeO layers are different, both interfaces have to be treated separately with different activation barriers.

Only limited data on tritium release from irradiated beryllium are available for the post-irradiation annealing results of Baldwin [1–3], and from the SIBELIUS

experiments [4]. Several models [5–10] have been proposed to explain the surface processes. They consider tritium transport processes at the surface from dissociative chemisorption and surface atom recombination, or direct transfer of tritium atoms between both the gas phase and the bulk. These models deal with only a few individual surface processes in the limiting cases of the surface coverage. However, each surface process plays an important role in tritium transport in beryllium under different surface conditions. The incorporation of the surface processes in the model was limited, since only a small amount of data is available on the activation energies of the surface processes.

The simplest surface processes were used in the initial version of BETTY [11] and the fundamental property data were derived from the analysis of experimental data. A key improvement of the model consists of a better characterization of the process at the surfaces and their linking to the bulk and pore regions as well as the treatment of the He bubble as the sink/source terms in the bulk.

This paper describes the new version of BETTY for tritium transport in irradiated beryllium, and its application to the analysis of recent SIBELIUS experimental data. A comparison of the results available for irradiated beryllium samples from the tritium release experiments with those predicted by the model is presented. In addition, to help interpret and plan future experimental data for fusion blanket applications, a parametric analysis for the variation of surface activation energies and diffusion coefficient is performed and the results of the analysis are presented and discussed.

2. Tritium transport mechanisms in the model BETTY

Release of tritium from the metal Be may be considered to take place in several stages: (1) a tritium atom generated in the bulk diffuses to the solid–gas interfaces, (2) it recombines with another atom and escapes as a molecule to the gas phase, and (3) it diffuses through the pore to the purge gas. Here the concern is with the surface process. Particular emphasis is placed on the different mechanisms by which two tritium atoms enter the bulk and/or the surface after a gas molecule has been dissociated, or conversely the mechanisms for recombination and release of two atoms initially in the bulk and/or the surface.

Conventional adsorption and release processes are expressed by four fluxes, f_1 through f_4 , as shown in Fig. 1. However, it was noted that surface saturation would

enhance the relative importance of alternative adsorption and release mechanisms in which one of the two tritium atoms moves directly between the molecular and solution states without being chemisorbed at the surface, as represented by fluxes f_5 and f_6 in Fig. 1. Recently, a third mechanism was developed, in which the adsorption and release occur with both atoms by-passing the chemisorption sites as depicted by fluxes f_7 and f_8 in Fig. 1.

The representative incoming fluxes f_i ($i = 1, 5, 7$) from the gas phase in each mechanism were investigated and a parametric analysis was performed in order to find the relative importance of these fluxes in Ref. [12]. The surface fluxes f_i ($i = 1, \dots, 4$) would be dominant for endothermic Be, and all the surface processes f_i ($i = 1, \dots, 8$) would be considered for exothermic BeO. Therefore, a complete treatment of the surface would involve all possible processes for arbitrary surface coverage. If surface coverages are not included in the model, however, only two fluxes f_7 and f_8 can be considered at the solid–gas surfaces in both endothermic Be and exothermic BeO.

Helium bubbles are the most likely traps in neutron irradiated Be. As tritium is formed in the Be lattice, it diffuses to sites of lower energy, which in this case are thought to be the He bubbles, assuming that He bubbles exist only inside the Be bulk. When tritium was held in the lattice or in simple traps, the conventional theory for the filling and emptying of traps [13,14] implied that the rate limiting constraints would be the

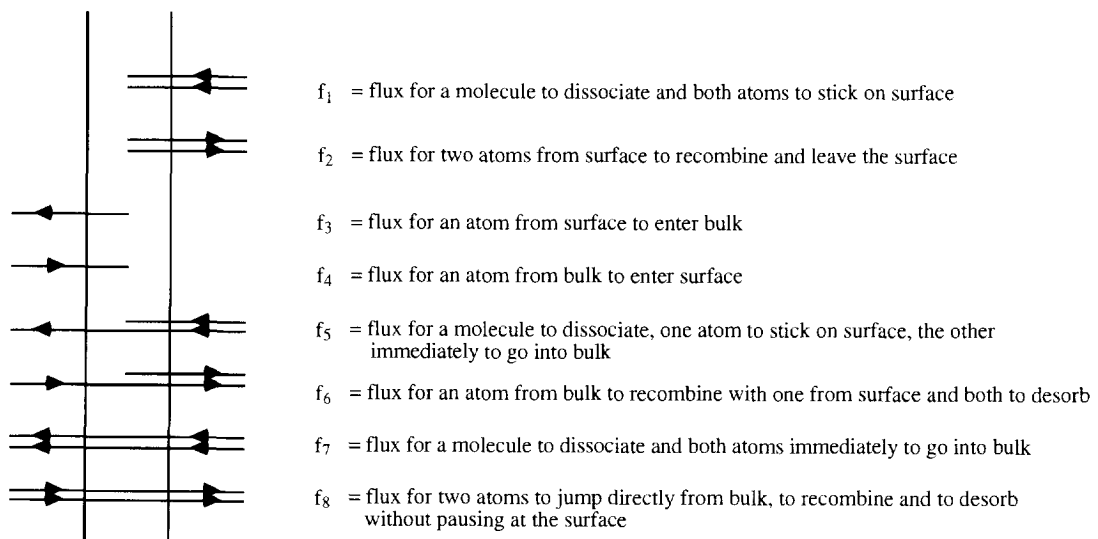


Fig. 1. Schematic diagram of surface fluxes at the gas–surface–Be metal interface.

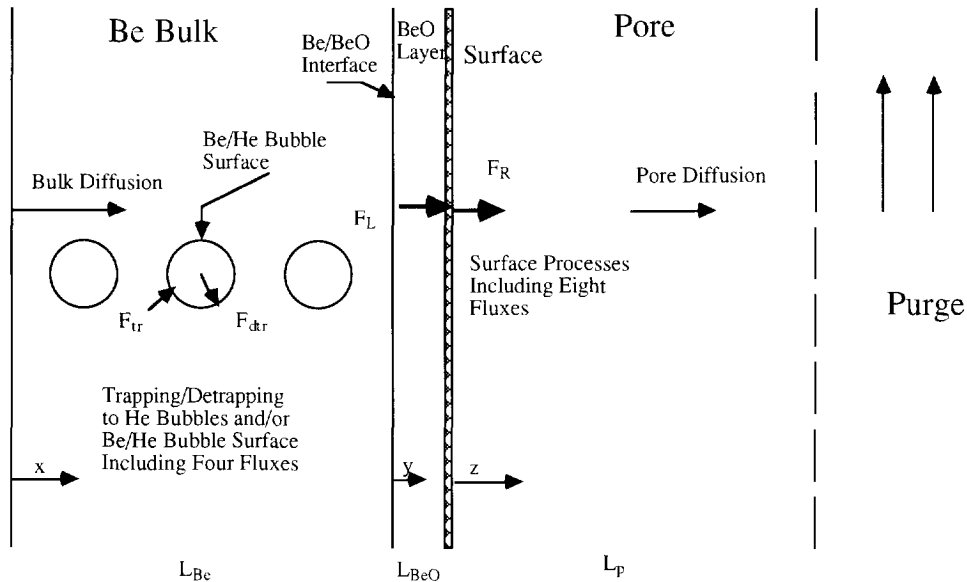


Fig. 2. Schematic diagram of the integrated model (BETTY) for tritium transport in beryllium.

number and energy of traps and the diffusivity. Richards et al. [9] considered He bubble traps as a void and the Be–He bubble surface as a bare, i.e. zero surface coverage ($\theta = 0$), metal surface. However, He bubbles are not simple traps, and tritium at the Be–He bubble interface experiences an environment similar to that on a Be–gas surface. It is believed that since tritium exists as molecules when it collects in bubbles the molecules can dissociate and adsorb to the surface of the bubble and escape by going into solution and diffusing to the surface and vice versa.

When these surface processes are included at the Be–He bubble interface, a potential energy diagram at the Be–He bubble surface is exactly the same as that at the Be–gas surface. Because the tritium concentration around each He bubble is different, the surface coverage at each Be–He bubble is different and can be a function of position such as the tritium concentration inside the bulk. A way to include He bubble traps in the continuum bulk diffusion equation is to treat He bubbles as a source/sink term in the diffusion equation.

In addition to the transport mechanism of the initial version of the model, an integrated model for tritium release from the irradiated beryllium includes the surface processes and irradiation-induced He bubbles as shown in Fig. 2. In this model, F_{tr} and F_{dtr} are the net fluxes of trapping and detrapping to the Be–He bubble surface, and F_L and F_R are the net fluxes at the bulk–

gas surface. A more detailed description of the model and governing equations used in the model can be found in Ref. [12].

3. Existing property data

Several parameters are specified including the activation energies of different surface processes and the bulk diffusion coefficient. Although all the specific activation energies for the surface processes have not been determined experimentally for Be, experimental data on the adsorption activation energy, solution energy and desorption activation energy for the hydrogen isotopes are available.

Swansiger [15] determined tritium solubility in high purity, Be at temperatures from 285 to 510 °C. The solubility shows that Be is endothermic and has a high value of solution energy E_s . Lossev and Küppers [16] estimated the hydrogen adsorption activation energy in Be E_{ads} to be larger than 1 eV based on measurements of the potential well for hydrogen below the Be surface. The hydrogen desorption activation energy E_{des} was obtained using thermal desorption spectroscopy (TDS) by Ray et al. [17]. For associative desorption, second-order desorption kinetics was included by assuming that E_{des} is a linear function of coverage θ : $E_{des} = E_1 + E_2\theta$, where E_1 and E_2 are constant. This

Table 1
Reference property data and input parameters

| | Beryllium | | Beryllium oxide | |
|--|-----------------------------------|------|-----------------------------------|------|
| Pre-exponential diffusion coefficient D_0 ($\text{m}^2 \text{s}^{-1}$) | 4.56×10^{-7} | [11] | 6.28×10^{-16} | [11] |
| | | | 1.11×10^{-6} | [20] |
| Activation energies (kJ mol^{-1}) | | | | |
| Diffusion E_D | 104.63 | [11] | 53.35 ($< 650^\circ\text{C}$) | [11] |
| | | | 219.81 ($> 650^\circ\text{C}$) | [20] |
| Bulk adsorption E_B | 55.34 | [11] | 28.75 | [11] |
| Solution E_s | 96.48 | [15] | 77.18 | [19] |
| Adsorption E_{ads} | 48.24 | [16] | ≈ 0 | [9] |
| Desorption E_{des} | $38.59 + 18.8\theta$ | [17] | $Q_{\text{ads}} + E_{\text{ads}}$ | |
| Heat of adsorption Q_{ads} | $E_{\text{des}} - E_{\text{ads}}$ | | $E_{\text{des}} - E_{\text{ads}}$ | |

expression is different from that for LiAlO_2 experiments, where E_{des} is a linear function of $\ln(\theta)$ [18]. Owing to the absence of tritium activation energies in Be, hydrogen activation energies are used for the analysis. A sensitivity analysis is required to verify the effect of a change in these parameters on the overall results.

From the analysis of the previous experimental data [11], bulk adsorption activation energies E_B for Be and BeO can be estimated from the second-order desorption coefficient, where the surface was not included and only two surface fluxes f_7 and f_8 were considered at the burst release stage. Also, the tritium diffusion coefficients of Be and BeO obtained from Ref. [11] were used in this analysis.

Macaulay-Newcombe and Thompson [19] found the second-order recombination kinetics at the BeO surface and showed that BeO is exothermic material and the solubility of deuterium in BeO was estimated. For most exothermic BeO, the adsorption activation energy is almost zero [9]. Since there are no available data for the desorption activation energy in BeO, a sensitivity analysis is needed to estimate the activation energy.

Assuming that the surface fluxes can be reasonably characterized as shown above, the model can be used to analyze the recent experimental data. The robustness of the analysis can also be verified by determining through sensitivity analyses the effect on the results of varying key reference input parameters. The reference input parameters assumed for the analysis are summarized in Table 1.

4. Analysis of experimental data

In the SIBELIUS experiments [4], the effects of tritium trapping in He bubbles and tritium retardation in

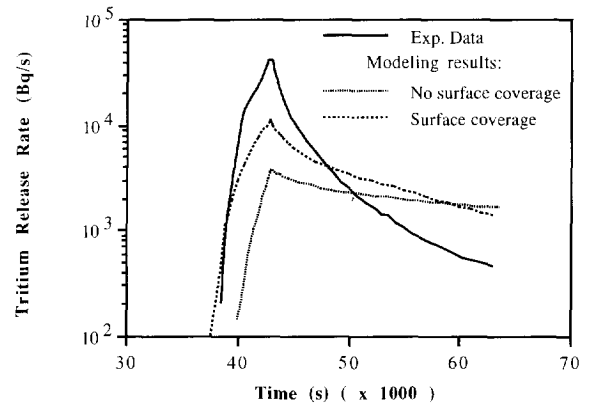


Fig. 3. Comparison of BETTY results with SIBELIUS experimental data [4] for tritium release from the irradiated beryllium under a constant heating rate. The effect of surface coverage on the modeling results is shown.

the BeO layer on tritium release would be relatively less important than the other tritium transport mechanisms, such as bulk diffusion and/or surface processes at the solid-gas interface, owing to the very low oxygen content (less than 300 ppm BeO) and low irradiation fluence ($6 \times 10^{20} \text{ n cm}^{-2}$). So, in this analysis only pure Be bulk diffusion and surface processes are considered.

Based on the limited available data shown in Table 1, the modeling results are compared with the SIBELIUS experimental data in Fig. 3. When the surface coverage is not considered, only two surface fluxes, f_7 and f_8 , are included in the model with the desorption activation energy of $2E_B$, which is the necessary energy for two tritium atoms to recombine and to desorb from the bulk. When the surface coverage is considered, how-

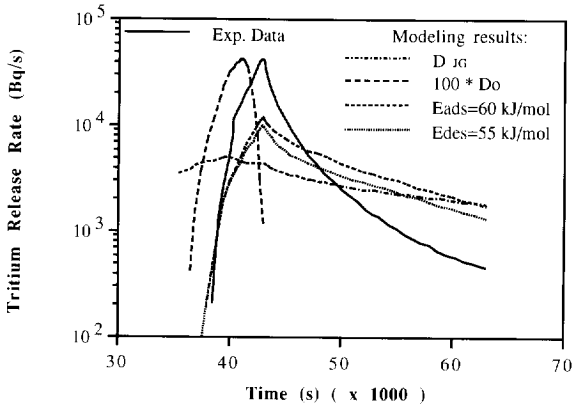


Fig. 4. Comparison of BETTY results with SIBELIUS experimental data [4] for tritium release from the irradiated beryllium under a constant heating rate. The effect of diffusion coefficient and E_{ads} and E_{des} on the modeling results is shown.

ever, four surface fluxes f_i ($i = 1, \dots, 4$) are considered. The activation energy of the flux f_4 , E_B , is the necessary energy for a tritium atom to jump to a surface site, and the activation energy of flux f_2 , $2E_{\text{des}}$, is the necessary energy for two tritium atoms to recombine and desorb from the surface. The fact that these desorbing activation energies are much smaller than $2E_B$ (see Table 1) means that the surface can promote tritium release from the material. Therefore, when the surface coverage is considered, the tritium releases faster and the shape of the modeling results is closer to the experimental data as shown in Fig. 3.

The SIBELIUS experimental data have a major uncertainty in the absolute values of the measured tritium release rate owing to the uncertainty of the calibration of the ionization chamber, and the absolute values could be too high by a factor of 2.6. A minor uncertainty has been found in the shape of the experimental data within several tens of per cent [21]. So, the magnitude of the peak of modeling results with surface coverage (see Fig. 3), which is about three times lower than that of experimental data, can be reached by the data within a few tens of per cent.

Since the property data assumed in this analysis are not dominant values, a sensitivity analysis for the variation of surface activation energies and diffusion coefficient was performed and the results are shown in Fig. 4. First of all, the tritium diffusion coefficients vary in a wide range: the tritium diffusion coefficient D_{Be} used in this analysis is the lower bound and Jones and Gibson's value D_{JG} is the upper bound [11]. The

modeling results with D_{JG} are shown in Fig. 4. Since the activation energy of diffusion E_D for D_{JG} is smaller than that of D_{Be} , large amounts of tritium are released at lower temperatures reaching the peak earlier, compared with the experimental data.

Based on the input data shown in Table 1, a 100 times larger value of the pre-exponential diffusion coefficient D_0 is applied to the model and the result is also shown in Fig. 4. High D_0 means fast diffusion, which shows that the peak will be reached earlier than indicated by the experimental data. Therefore, D_0 and E_D values shown in Table 1 can only reproduce the position of the peak of the tritium release from beryllium.

Since the adsorption activation energy E_{ads} used as the reference value in Table 1 is the lower limit of E_{ads} , BETTY was run for the high value $E_{\text{ads}} = 60 \text{ kJ mol}^{-1}$ in order to ascertain the effect of E_{ads} on the results, and the results are shown in Fig. 4. The overall trend is the same as the result shown in Fig. 3. For the coverage $\theta \leq 0.6$, the desorption activation energy E_{des} is smaller than E_{ads} , i.e. the heat of adsorption Q_{ads} is less than zero. In order to keep Q_{ads} positive, a constant maximum value of $E_{\text{des}} = 55 \text{ kJ mol}^{-1}$ was applied to BETTY and the result is shown in Fig. 4. Again, minimal effects (approximately 1% change) were observed on the modeling results. Overall, the sensitivity analyses indicated that over a reasonable range of various activation energies, the modeling results do not change significantly, and confirmed the validity of the bulk tritium diffusion coefficient shown in Table 1.

5. Conclusions

Being reinforced with surface processes, BETTY reproduced the SIBELIUS experimental data on tritium release from irradiated beryllium reasonably well. The surface processes at the bulk–gas interface improved the tritium release from beryllium with lower desorption activation energies. For given surface activation energies based on past experiments and analysis, the diffusion coefficient D_{Be} was verified and it is suggested that this value of D_{Be} be used for future blanket design analysis. Sensitivity analysis indicated minimal change in the modeling results when E_{ads} and E_{des} were varied over a realistic range. A code improvement is needed in order to investigate the effect of tritium trapping and detrapping in He bubbles and the kinetics of the BeO surface layer, based on existing or additional experimental data.

References

- [1] M.C. Billone, C.C. Lin and D.L. Baldwin, Tritium and helium behavior in irradiated beryllium, *Fusion Eng.* 19 (1991) 1707–1714.
- [2] D.L. Baldwin, O.D. Slagle and D.S. Gelles, Tritium release from irradiated beryllium at elevated temperatures, *J. Nucl. Mater.* 179–181 (1991) 329–334.
- [3] M.C. Billone and D.L. Baldwin, Tritium and helium behavior in porous beryllium, *Proc. Int. Workshop on Ceramic Breeder Blanket Interactions*, Tokyo, January 1993.
- [4] W. Dienst, D. Schild and H. Werle, Tritium release of Li_4SiO_4 , Li_2O and beryllium and chemical compatibility of beryllium with Li_4SiO_4 , Li_2O and steel (SIBELIUS irradiation), KfK Report 5109, December 1992 (Kernforschungszentrum Karlsruhe).
- [5] F. Waelbroeck, I. Ali-Khan, K.J. Dietz and P. Weinhold, Hydrogen solubilization into and permeation through wall materials, *J. Nucl. Mater.* 85–86 (1979) 345–349.
- [6] M.I. Baskes, A calculation of the surface recombination rate constant for hydrogen isotopes on metals, *J. Nucl. Mater.* 92 (1980) 318–324.
- [7] M.A. Pick and K. Sonnenberg, A model for atomic hydrogen–metal interactions—application to recycling, recombination and permeation, *J. Nucl. Mater.* 131 (1985) 208–220.
- [8] P.M. Richards, Surface-limited hydrogen release and uptake in metals, *J. Nucl. Mater.* 152 (1988) 246–258.
- [9] P.M. Richards, S.M. Myers, W.R. Wampler and D.M. Follstaedt, Mechanism of surface-limited release of hydrogen from oxidized metals, *J. Appl. Phys.* 65(1) (1989) 180–185.
- [10] A.R. Raffray, S. Cho and M.A. Abdou, Modeling of tritium transport in ceramic breeder single crystal, *J. Nucl. Mater.*, in press.
- [11] S. Cho, A.R. Raffray and M.A. Abdou, Modeling of tritium release from beryllium in fusion blanket applications, Sixth Int. Conf. on Fusion Reactor Materials (ICFRM-6), September 1993.
- [12] S. Cho, Modeling and analysis of tritium behavior in ceramic breeder single crystal and beryllium in fusion blanket applications, PhD Dissertation, University of California, Los Angeles, CA, 1994.
- [13] G.R. Longhurst, Observing diffusivity and traps for tritium in metals by thermal transient tests, EG&G Idaho Inc., 1988 (EG&G Idaho Inc.)
- [14] M.I. Baskes, DIFFUSE 83, SAND83-8231/UC-32, 1983 (Sandia National Laboratory).
- [15] W.A. Swansiger, Tritium solubility in high purity beryllium, *J. Vac. Sci. Technol. A* 4(3) (1986) 1216–1217.
- [16] V. Lossev and J. Küppers, Interaction of hydrogen atoms with beryllium (0001) surfaces, *J. Nucl. Mater.* 196–198 (1992) 953–957.
- [17] K.B. Ray, J.B. Hannon and E.W. Plummer, An experimental study of hydrogen adsorption on beryllium, *Chem. Phys. Lett.* 171 (1990) 469–474.
- [18] A.K. Fischer and C.E. Johnson, Measurement of adsorption in the $\text{LiAlO}_2\text{--H}_2\text{O(g)}$ system, *Fusion Technol.* 15(2B) (1989) 1212–1216.
- [19] R.G. Macaulay-Newcombe and D. A. Thompson, The effects of surface contamination on absorption and desorption of deuterium in beryllium and beryllium oxide, Sixth Int. Conf. on Fusion Reactor Materials (ICFRM-6), September, 1993.
- [20] J.D. Fowler, D. Chandra, T.S. Tileman, A.W. Payne and K. Verghese, Tritium diffusion in Al_2O_3 and BeO , *J. Am. Ceram. Soc.* 60(3–4) (1977) 155–161.
- [21] H. Werle, Personal communication, April 1994.