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Deuterium release from plasma-exposed beryllium during thermal desorption

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Abstract

An analytic solution is obtained for the thermal desorption spectrum of deuterium released from beryllium samples containing a mixed-material surface layer following exposure to a steady-state, high flux plasma. The analytical results are used to interpret experimental data that showed two separate deuterium release peaks. By comparing the calculations and measurements, the activation energy for diffusion of deuterium in beryllium is estimated and found to be higher than values previously reported in the literature. It is also found that the desorption spectrum is determined by the temperature ramping rate, the deuterium diffusion depth, and the material diffusivity. The fact that the analytical model agrees well with large-scale TMAP4 calculations suggests that desorption in this case is not strongly dependent on boundary conditions or recombination-limited surface kinetics. © 1998 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

The tritium inventory contained in plasma-facing components and the permeation of tritium through the first wall are critical safety issues facing the development of fusion energy [1]. The transport of hydrogen in a material is governed by various physical parameters such as its diffusivity, solubility, trapping energy, and permeability. Beryllium has been selected as a primary plasma-facing material in the design of the ITER fusion experiment [2] because of its low atomic number and low self-sputtering coefficient, among other properties [3]. Unfortunately, literature values for the diffusivity, solubility, and trapping energy of hydrogen in beryllium show a high degree of variability [4]. This scatter in the data is often attributed to factors such as variations in the method of fabrication and variability in the crystalline phase, grain size, types of impurities, variable surface conditions, and so on. Beyond this large scatter in the data, there is not a clear understanding of the mechanism of hydrogen desorption from a beryllium surface [5].

In this paper, an analytic solution is obtained for the rate of deuterium desorption from a thin, planar specimen (in this case, 0.16 cm thick beryllium disks) subjected to a ramp increase of its temperature. The desorption experiment follows exposure of the sample itself to a steady-state, high flux deuterium plasma produced in the PISCES fusion facility [6]. A thin impurity layer is observed to form on the surface of the sample during the exposure. This layer has been extensively characterized [7]. Following the exposure, the specimen is transported to a vacuum outgassing chamber in order to measure the amount of deuterium retained in the beryllium specimen by use of thermal desorption spectrometry (TDS). As the specimen temperature is ramped linearly upwards in time using an IR heater to 650°C, gas desorbs and the partial pressure of deuterium-containing molecules such as HD and D_2 is measured using a quadruple mass analyzer (QMA).

Modeling the desorption experiment permits one to identify important parameters that determine the desorption spectrum. The analytical results are compared

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with calculations using the TMAP4 computer code [8] and are found to be in a good agreement. The results allow us to interpret the observed deuterium desorption spectra that has been measured experimentally [9].

2. Theoretical modeling

The one-dimensional transport of deuterium in a substance can be described by the diffusion equation

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D(x,t)\frac{\partial C}{\partial x}\right), \tag{1}$$

where $C(x,t)$ is the deuterium concentration in the substance, $D(x,t)$ is the diffusivity of deuterium atoms, t is time, and x is the distance. In general, the diffusivity is given [10] as

$$D(T) = D_0 \mathrm{e}^{-\varepsilon/kT}, \tag{2}$$

where D_0 is the asymptotic diffusion coefficient, ε is the activation energy for deuterium atom diffusion, k is the Boltzmann constant, and T is temperature. During thermal desorption experiments [6], the temperature of a sample is raised linearly in time inside a quartz tube. Since the thermal conductivity of beryllium is high, it is reasonable to assume that the sample temperature is spatially uniform during the desorption process. As the sample temperature increases with time, the diffusivity also varies. In the experiments, the specimen temperature is linearly ramped up to 650°C. As such, the relationship between the sample temperature and time is well described by

$$t = aT + b \tag{3}$$

during the ramp itself. The constants a and b are determined by the heating scheme.

The dependence of deuterium concentration on time, $C(x,t)$, can be expressed as well as a function of space and of the sample temperature, i.e., as $C(x,T)$. Then, Eq. (1) becomes

$$\frac{1}{a}\frac{\partial C}{\partial T} = D(T)\frac{\partial^2 C}{\partial x^2}. \tag{4}$$

Using the method of separation of variables, with

$$C(x,T) = X(x)Y(T), \tag{5}$$

the solution is

$$Y(T) = \text{const}\ \exp\left[a\lambda^2 D_0 \frac{\varepsilon}{k}\int_{\varepsilon/kT_0}^{\varepsilon/kT}\frac{\mathrm{e}^{-v}}{v^2}\,\mathrm{d}v\right], \tag{6}$$

where λ is the separation constant and T_0 is the initial temperature. The integration term in the bracket can be calculated numerically. The solution for $X(x)$ is

$$X(x) = A\ \sin\ \lambda x + B\ \cos\ \lambda x. \tag{7}$$

Assume now that the deuterium concentration is initially uniformly at a saturation density, C_0, in the beryllium specimen to depth, l, following deuterium plasma exposure. Assume also that the concentration is zero on the surface and at $x = l$. This implies boundary conditions

$$C = C_0, \quad -l < x < 0, \quad T = T_0, \tag{8}$$

$$C = 0, \quad x = 0, \quad x = l, \quad T > T_0. \tag{9}$$

Using these boundary conditions and the orthogonality properties of trigonometric functions, we find the total solution to be

$$C(x,T) = \frac{4C_0}{\pi}\sum_{m=0}^{\infty}\frac{1}{2m+1}\sin\left(\frac{(2m+1)\pi x}{l}\right) \exp\left[a\left(\frac{(2m+1)\pi}{l}\right)^2 D_0\frac{\varepsilon}{k}\int_{\varepsilon/kT_0}^{\varepsilon/kT}\frac{\mathrm{e}^{-v}}{v^2}\,\mathrm{d}v\right], \tag{10}$$

where m takes values $0, 1, 2, \ldots$

If Fick's law governs the release of deuterium from the surface $x = 0$, then the desorption rate is

$$\begin{aligned} J_0 &= -D(T)\frac{\partial C}{\partial x}\bigg|_{x=0} \\ &= -\frac{4C_0}{l}D_0\mathrm{e}^{-\varepsilon/kT} \\ &\quad\times\sum_{m=0}^{\infty}\exp\left[a\left(\frac{(2m+1)\pi}{l}\right)^2 D_0\frac{\varepsilon}{k}\int_{\varepsilon/kT_0}^{\varepsilon/kT}\frac{\mathrm{e}^{-v}}{v^2}\,\mathrm{d}v\right], \\ m &= 0, 1, 2, 3, \ldots \end{aligned} \tag{11}$$

Clearly, we are neglecting effects such as surface recombination and trapping, but comparison with experiment will help determine whether or not these effects are important for the deuterium–beryllium system.

In Eq. (13), the pre-exponential factor (D_0) and the activation energy (ε) are intrinsic properties of a material, but the temperature ramping rate (a) and the deuterium diffusion depth (l) are controllable or measurable.

3. Results and discussion

The value of the diffusivity of deuterium in beryllium that was measured by Abramov et al. [11] has been recommended as the value to use by Dolan and Anderl [4]. For the calculations in this study, their recommended pre-exponential factor ($D_0 = 8.0 \times 10^{-5}$ cm^2 s^{-1}) is also used. The sample temperature ramping rate is taken to be 20 K per minute (i.e., $a = 3.0$ s K^{-1}), which is the value used in the experiments reported in Ref. [8]. As noted, the specimen temperature is increased linearly to 923 K and then held constant.

In Fig. 1, we show the results of calculations of the normalized desorption spectra for a case where the

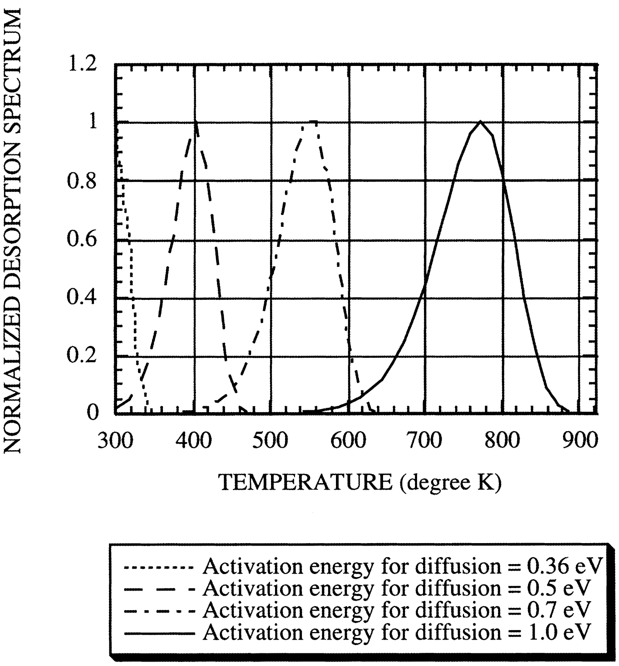

Fig. 1. Normalized deuterium desorption spectra calculated from the analytic solution ($m = 0$) for various activation energy for diffusion, assuming that the deuterium-diffused depth is 2.0 μm.

deuterium diffusion depth of 2.0 μm and the activation energy for diffusion is varied from 0.36 to 1.0 eV. For the results in Fig. 1, only the principal spatial mode ($m = 0$) is considered. As can be seen, the desorption spectrum is quite sensitive to the activation energy and the peak of the release shifts to higher temperatures as the activation energy is increased from 0.36 eV, as recommended in Ref. [11], to 1.0 eV.

The sensitivity of the desorption spectrum to the value of the deuterium diffusion depth is shown in Fig. 2, with this depth varying from 0.2 to 10 μm. Again, only the $m = 0$ mode is considered. The smaller value of 0.2 μm approximately corresponds to the thickness of an impurity layer that has been found in experiments [7] to form on a beryllium surface when the specimen is maintained at high temperature during plasma exposure. The highest value of 10 μm is the estimated deuterium diffusion depth in bulk beryllium, determined from $\sqrt{Dt}$, and where t is the plasma exposure time. An activation energy of 1 eV is used for the results shown in Fig. 2. As expected, the peak deuterium desorption rate is delayed in time as the deuterium saturation depth increases. However, comparing the results in Figs. 1 and 2, we note that the spectrum appears to be less sensitive to the deuterium diffusion depth than to the activation energy for diffusion.

The results from the analytic solution have been compared with results obtained using the TMAP4 computer code. As earlier, the activation energy is varied, now from 0.36 to 1.2 eV, and the deuterium diffusion depth is also varied, from 0.2 to 20 μm. The analytical and computer code results are found to be in a good agreement with each other. As an example, using an activation energy of 1.0 eV and a deuterium diffusion depth of 2.0 μm, we show in Fig. 3 the results from the analytic solution and from the TMAP4 code. Two plots are shown for the analytic solution, one using only the principal mode ($m = 0$) and the other summing spatial modes up to $m = 4$. The analytic results using more spatial modes yields a somewhat better fit to the TMAP4 code result, a reasurring result. Since the boundary conditions associated with the analytical results imply no surface concentration, that same boundary condition was used in the TMAP4 code runs.

Let us now turn to a comparison of the analytic results with experiment. The experiments are those in which the thermal desorption spectra from a beryllium specimen is obtained following sample exposure to deuterium plasma bombardment in the PISCES-B facility [7]. The samples are removed and transferred to perform the thermal desorption experiments.

It was found by Won et al. [7] that a thin (~0.2 μm) impurity layer is formed on a beryllium surface during exposure to a deuterium plasma containing about 1% carbon impurity concentration when the specimen is maintained at temperatures above about 250°C. The deuterium (as HD and D_2) desorption spectrum, mea-

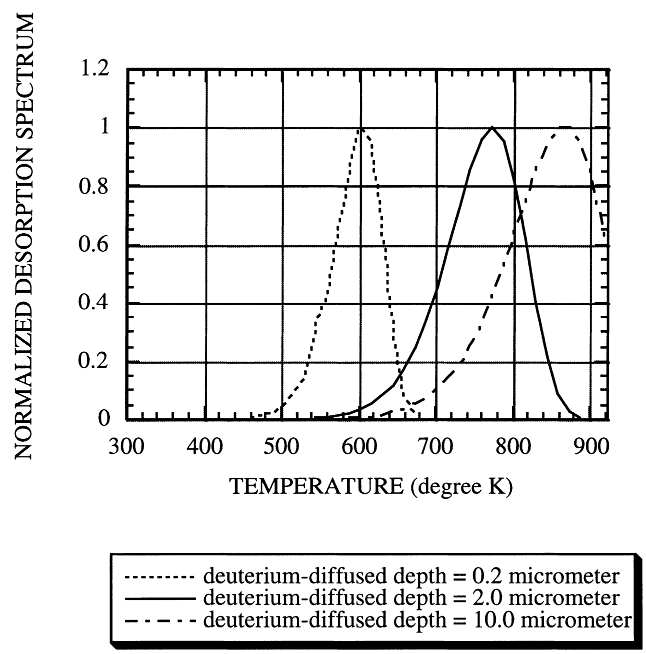

Fig. 2. Normalized deuterium desorption spectra calculated from the analytic solution ($m = 0$) for various deuterium-diffused depth, assuming that the activation energy for diffusion is 1.0 eV.

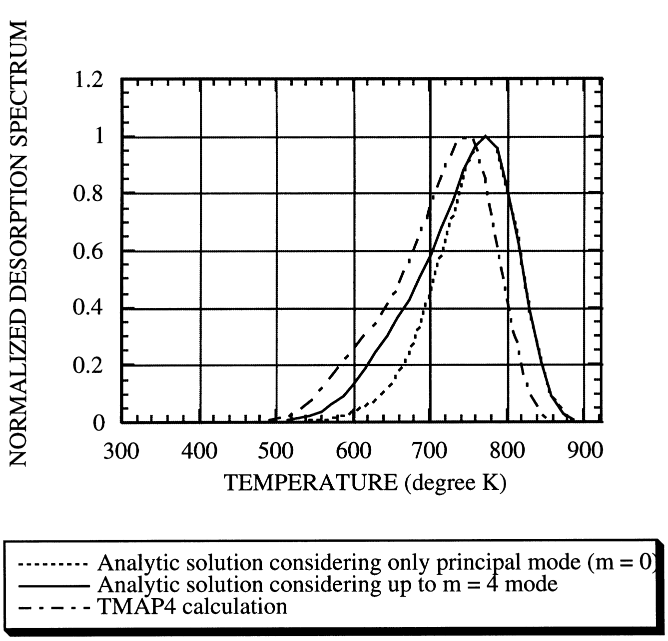

Fig. 3. Comparison of the analytic solutions (principal mode and up to $m = 4$ mode) and TMAP4 calculation, assuming the activation energy of 1.0 eV and the deuterium-diffused depth of 2.0 μm.

sured post-exposure, of gas evolved from such a beryllium specimen was found to exhibit two distinct, separate release peaks. By resolving the desorption spectrum as the sum of two Gaussians, Conn et al. [9] interpreted the first peak, at around 340°C, as the release of deuterium from the impurity layer and the second peak, at around 470°C, as the release of deuterium from bulk beryllium.

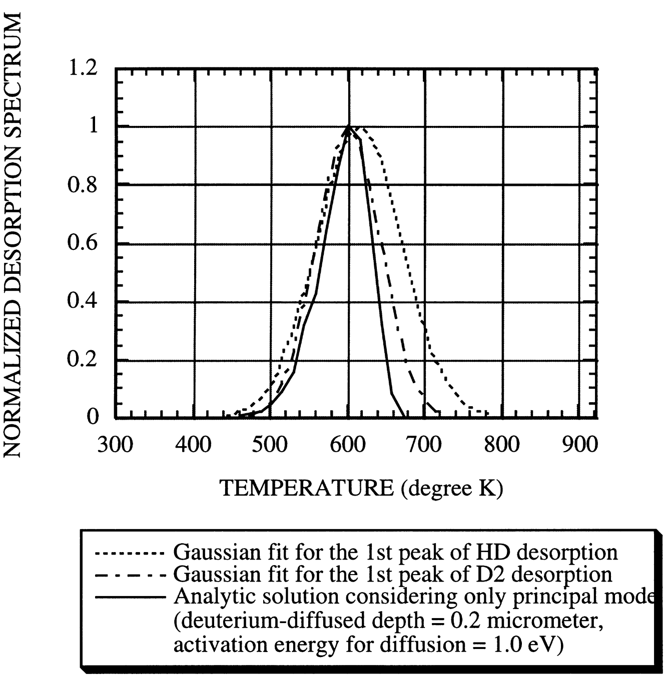

Fig. 4. Comparison of the analytic solution and Gaussian-fit experimental data measured in PISCES during thermal desorption experiment [9] for the 1st peaks of HD and D_2 spectra, presumed to be a release from a surface impurity layer on beryllium formed during plasma exposure.

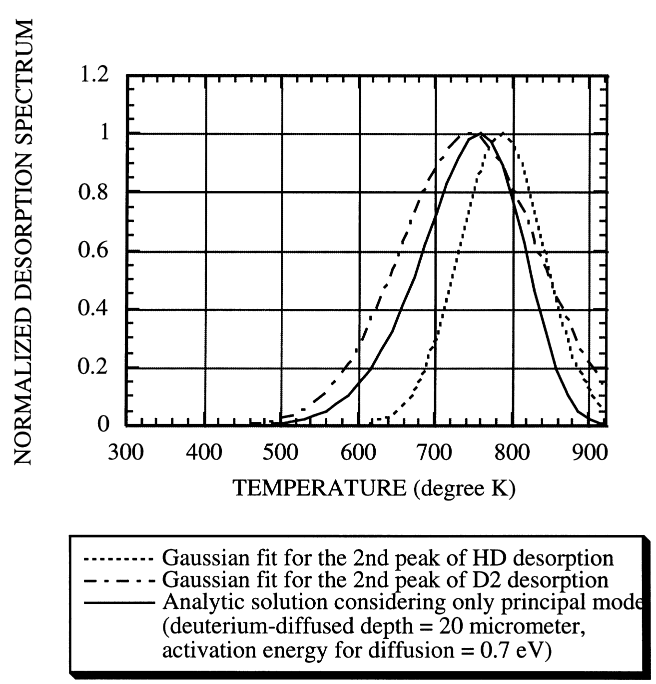

Fig. 5. Comparison of the analytic solution and Gaussian-fit experimental data measured in PISCES during thermal desorption experiment [9] for the 2nd peaks of HD and D_2 spectra, presumed to be a release from the bulk beryllium.

In Fig. 4, the Gaussian fits for the first peaks of HD and D_2 are compared with the result of the analytic solution to Eq. (4) (using only the $m = 0$ spatial mode), assuming that the impurity layer thickness of 0.2 μm and that the activation energy for diffusion is 1.0 eV. There is a good general agreement, although the Gaussian fits have wider FWHMs, especially for HD molecules. In Fig. 5, the analytic solution ($m = 0$ mode) is compared with the Gaussian fits for the second desorption spectrum peaks of HD and D_2, setting the activation energy at 0.7 eV. The deuterium diffusion depth is estimated to be 20 μm, consistent with the deuterium plasma conditions and the expected ion bombarding energy, taking account of the Debye sheath. Again, the analytic result is in reasonably good agreement with the measurements.

It seems clear from these results that the activation energy for diffusion of deuterium in beryllium must be higher than the value reported by Abramov et al. [11], assuming that the pre-exponential factor is correct.

4. Conclusion

An analytic solution is obtained for the thermal desorption spectrum of deuterium released from beryllium samples containing a mixed-material surface layer following exposure to a steady-state, high flux plasma. The validity of applying the proposed analytic solution to determine the deuterium desorption spectrum from such samples is established by the ability of the model to yield good agreement with experiment over a wide range of temperature ramping rates. As such, the analytical results are used to interpret experimental data that showed two separate deuterium release peaks. By comparing the calculations and measurements, the activation energy for diffusion of deuterium in beryllium is estimated and the results suggest that this energy must be higher than the value reported by Abramov et al. [11]. It is also found that the desorption spectrum is determined by the temperature ramping rate, the deuterium diffusion depth, and the material diffusivity. The fact that the analytical model agrees well with large-scale TMAP4 calculations suggests that desorption in this case is not strongly dependent on boundary conditions or recombination-limited surface kinetics.

References

[1] R.A. Langley, Fusion Technol. 27 (1995) 41.

[2] ITER Joint Central Team, J. Nucl. Mater. 212&213 (1994) 3.

[3] K.L. Wilson, R.A. Causey, W.L. Hsu, B.E. Mills, M.F. Smith, J.B. Whitley, J. Vac. Sci. Technol. A8 (1990) 1750.

[4] T.J. Dolan, R.A. Anderl, Assessment of Database for Interaction of Tritium with ITER Plasma Facing Materials, Report ITER/93/US/TE/SA-10, Idaho National Engineering Laboratory, 1994 pp. 5–20.

[5] K.L. Wilson, R. Bastasz, R.A. Causey, D.K. Brice, B.L. Doyle, W.R. Wampler, W. Moller, B.M.U. Scherzer, T. Tanabe, in: Atomic and Plasma–Material Interaction Data for Fusion, IAEA, Vienna, 1991, p. 35.

[6] R.P. Doerner, A. Grossman, S. Luckhardt, F.C. Sze, R. Seraydarian, D.G. Whyte, R.W. Conn, J. Nucl. Mater., (1998) in press.

[7] J. Won, F.E. Spada, R. Boivin, R. Doerner, S. Luckhardt, F.C. Sze, R.W. Conn, J. Nucl. Mater. 241–243 (1997) 1110.

[8] G.R. Longhurst, D.F. Holland, J.L. Jones, B.J. Merrill, TMAP4 User's Manual, Report EGG-FSP-10315, Idaho National Engineering Laboratory, 1992.

[9] R.W. Conn, R.P. Doerner, J. Won, Fusion Eng. Design 37 (1997) 481.

[10] D.R. Olander, Fundamental Aspects of Nuclear Reactor Fuel Elements, Technical Information Center, US Department of Energy, Washington, DC, 1976, p. 77.

[11] E. Abramov, M.P. Riehm, D.A. Thomson, J. Nucl. Mater. 175 (1990) 90.