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DIFFUSION/DESORPTION OF TRITIUM
FROM IRRADIATED BERYLLIUM

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ABSTRACT

Stepped-thermal-anneal tritium-release measurements at 573 up to 1173 K have been performed on irradiated Be test materials, fabricated and irradiated to meet conditions relevant to the International Thermonuclear Experimental Reactor (ITER). A combined diffusion/desorption model for tritium release allows determination of diffusion coefficients and desorption-rate constants in the mixed-mechanism regime where both diffusion and surface desorption appear to be rate-limiting. The effective tritium diffusivities (m^2/s) for these materials, and also from new data analysis of previously reported fully dense material, were found to be

$$81\% \text{ TD Be: } 1.7 \times 10^{-11} \exp(-3.5 \text{ kJ/mol/RT})$$

$$99\% \text{ TD Be: } 1.6 \times 10^{-10} \exp(-9.5 \text{ kJ/mol/RT})$$

$$100\% \text{ TD Be: } 1.4 \times 10^{-10} \exp(-11.5 \text{ kJ/mol/RT})$$

Tritium release data for both the 81% TD and the 99% TD sample were matched reasonably well by the diffusion/desorption model. The model provides evidence for a changing mechanism over both temperature and density, but indicates that diffusion is the primary mechanism with a small and changing contribution from surface desorption.

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1. Introduction

Pacific Northwest Laboratory^a (PNL) has recently completed ³H and He release studies on two beryllium test materials, which were fabricated and irradiated to meet conditions relevant to the International Thermonuclear Experimental Reactor (ITER). These test samples were fabricated to 81% and 99% theoretical density (TD), have moderate BeO content, and were irradiated at low temperature to moderate fast-neutron fluence. Stepped thermal anneal tritium release tests, at 573 to 873 K, and in one case up to 1173 K, have been conducted, and the results used to determine ³H diffusion coefficients and desorption-rate constants. Additional data analysis was performed on previously reported release curves, resulting in diffusion coefficients for 100% TD Be. Tritium and He assay measurements of the 81% and 99% TD materials are reported and presented along with a comparison to similar data for the 100% TD Be, irradiated to high fast-neutron fluence.

A diffusion/desorption model for ³H release, based on slab geometry, was used to determine diffusion coefficients and surface desorption-rate constants in the mixed-mechanism regime where both mechanisms appear to be rate-limiting. The relative contribution of the two mechanisms is shown to change across the temperature range. The non-diffusional ³H "burst release" observed for all materials at the end of the anneals is also discussed.

2. Experimental

Stepped-anneal ³H release testing of both low-density (81%) and high-density (99%) Be irradiated in the Advanced Test Reactor (ATR), over 1500 h periods, was performed. A description of the fabrication and irradiation parameters of these two materials, along with a comparison to the 100% TD material reported earlier [1,2], is presented in Table 1. Using the experimental apparatus described previously [1], the 81% TD sample was heated at 573 to 873 K, in isothermal steps of 100 K, with about 400 h holds at each temperature. The 99% TD sample was heated in similar fashion from 573 to 973 K, then in 50 K steps to 1173 K. The hold times for the 973 to 1173 K range were 24 h per step to determine the presence and temperature of a burst release. Purge gas (He-0.1% H_2) at 100 scm³/min swept the wafer-shaped samples in a quartz system. Important modifications of the previously described

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apparatus [1] include eliminating the Zn reducer bed, adding 10 scm³/min moist air just before the CuO oxidizer column, and adding a pair of sequential ³HTO collection bubblers, replacing the molecular sieve columns.

In the case of the 81% TD sample, two independent release curves were obtained, generated by integration of the ionization chamber signal and by cumulative collection bubbler/liquid scintillation measurement. Because the 99% TD sample contained a small quantity of ³H, and had a comparatively large ionization chamber background level, the release curve was determined by cumulative collection bubbler/liquid scintillation measurement only. Cumulative collection bubbler data represent a "hard" data set, not requiring interpretation or correction. By comparison, integrated ionization chamber data represent a "soft" data set, requiring difficult time-dependent background-correction and possible correction due to calibration shifts. A dual data-collection scheme achieves a significant increase in the quality of information, allowing better data interpretation. In the first test with 81% TD Be, the integrated ionization chamber release curve was background-corrected to precisely fit the collection bubbler data set, while the 99% TD curve is based on collection bubbler results only. The ³H release fractions, $R(^3\text{H release})/I_0$ (initial inventory) versus time, at each of the temperatures, for the 81% and 99% TD Be specimens, are shown in Figure 1.

3. Diffusion/Desorption Model

A combined diffusion/desorption model is used to analyze the present ³H release data. The diffusion part of the model assumes that for a sample with initial ³H inventory, I_0 , the ³H released after long time, R_∞ , at an isothermal annealing temperature is uniformly distributed and available for transport in the bulk at the beginning of the anneal. The characteristic path length for diffusion is the half-width, ℓ , of the wafer-like samples. The presence of any BeO surface layer is not modeled. Thus the diffusivity determined by matching predictions to data is considered an "effective" diffusivity, D_{eff} . The surface-desorption part of the model assumes first-order kinetics, given the very high H/T ratio due to the protium-rich purge gas. Because the purge flow rate is much faster than the HT release rate, adsorption of ³H from the purge to the solid and solubility due to gas-solid equilibrium are treated as negligible. As the oxide layer at the surface may change during an anneal, the rate constant for this process is also to be considered an "effective" one, k_{eff} .

The mathematical expression of the diffusion/desorption model, solving for the release fraction, $f_r = R_t/R_\infty$, as function of time, is derived from Carslaw and Jaeger [3] as

$$f_r = 1 - 2 h^2 \sum_{n=1}^{\infty} \beta_n^{-2} [\beta_n^2 + h(h+1)]^{-1} \exp(-\beta_n^2 t/\tau_1) \quad (1)$$

where $\beta_n \tan \beta_n = h = k_{\text{eff}} \ell / D_{\text{eff}}$, $\tau_1 = \ell^2 / D_{\text{eff}}$, $D_{\text{eff}} = D_0 \exp(-Q_1/RT)$ in m^2/s , and $k_{\text{eff}} = k_0 \exp(-Q_2/RT)$ in m/s , t = time in s, ℓ = slab half-thickness in m, $R = 8.314 \times 10^{-3}$ kJ/mol-K, and T = temperature in K.

While no simple way exists to determine D and k from a data set with this equation, it is possible to vary D and k in a constrained manner ($h = k\ell/D$) until a best fit is obtained. The h -parameter acts as an indicator of rate-limiting mechanism, for as $h \rightarrow \infty$, diffusion becomes limiting, and as $h \rightarrow 0$, desorption becomes limiting. Mathematically, the long-time behavior of the ^3H release fraction can be expressed as

$$1 - f_r = 1 - A \exp(-Bt) \quad (2)$$

For diffusion controlled behavior, this implies that:

$$D \text{ in } \text{m}^2/\text{s} = B (4/\pi^2) \ell^2 \quad (2a)$$

For desorption-controlled release, the results imply:

$$k \text{ in } \text{m/s} = B \ell \quad (2b)$$

For combined diffusion-desorption controlled behavior, the results imply:

$$D \text{ in } \text{m}^2/\text{s} = B \ell^2 / \beta^2 \quad (2c)$$

where $\beta_1 \tan \beta_1 = h$, and β_1 is the lowest value of β_n .

A regression analysis of the long-time ^3H release data gives a value for the slope, B , for each data set. This result is used in Eq. 2c to determine a relationship between D and h . A spreadsheet model is then used to vary h from 0 to infinity in Eq. 1 (with the corresponding D vs. h constrained by Eq. 2c) until a best-fit of the whole time-history of the experimental f for a given temperature anneal is obtained. The surface desorption-rate constant, k , is then determined for each case from $k = Dh/\ell$. This method thus provides, with the graphically determined best h -parameter fit, the optimum D and k for the data set at each temperature.

4. Discussion

The summarized ^3H and He assay results and thermal-anneal release data collected over similar temperature ranges are listed in Table 2. The assay results for the low density (81%) and high density (99%) Be were expected to be similar for the two densities due to identical neutron fluence. However, the low density sample contained 23% less ^3H and 16% less He than the higher density sample. This difference is probably caused by loss of ^3H and He during irradiation through interconnected porosity of the low density material, even at the low irradiation temperature. This loss of He from the low density material suggests that the He generation rates established for the high density materials are probably more meaningful. Sannen and De Raedt [4] described ^3H and He measurements on high-density (99.5% TD) Be irradiated at low temperature (313 to 323 K) and at high fast neutron fluence levels (up

to 4×10^{22} n/cm², $E > 1$ MeV), material and conditions nearly identical to the 100% TD Be shown in Table 2. They reported a He generation rate of 4900 appm/ 10^{22} n/cm², very comparable to the 5300 ± 300 value for 100% TD Be in Table 2. The displayed ³H fractional release values can be seen as a matrix of temperature versus density. The trend in release at 573 to 773 K versus density shows the importance of porosity on ³H retention in Be. At 773 K, the low density Be displayed 89% ³H release, over an order of magnitude greater than for the 99% or the 100% TD sample.

Applying the diffusion/desorption model to the 81% and 99% TD data sets, a changing h-parameter, as a function of temperature and density, was observed, implying changing mechanisms with temperature and density. For both densities, the h-parameter was found to range from 1 to >100 for all temperatures, implying the rate-limiting mechanism ranged from mixed diffusion/desorption ($h=1$) to primarily diffusion ($h=>100$). In the high-density (99% TD) Be case, with increasing temperature from 573 to 773 K, the h-parameter decreased from 10 to 1, implying primarily diffusion at the lower temperatures and mixed diffusion and desorption at the higher temperature. In the low-density (81% TD) Be case, the reverse was observed, with the h-parameter increasing from 10 to >100 with increasing temperature, still indicating primarily diffusion with only a small contribution from desorption.

The resulting effective diffusivities, D_{eff} , are shown in Table 3, along with the effective desorption-rate constant, k_{eff} . A trend is seen, in the diffusion activation energy, Q_1 , with Be density, implying increasing temperature sensitivity of the diffusion mechanism to increasing density. The desorption activation energy, Q_2 , ranged from 4.6 to 18 kJ/mol, extending higher than Q_1 . The diffusion time constant, τ_1 , not to be confused with ³H residence time, ranges from 140 to 1250 h, showing relative insensitivity to Be density.

The results of this analysis indicate that diffusion is the primary rate-limiting mechanism. Thus, the selection of the proper diffusional dimension over this wide density range becomes important. At 100% TD, slab geometry, with its corresponding half-thickness, ℓ , was used, based on the metallic character of Be, instead of grain size or some average particle size. Compared with 10 to 40 μ grain size, 2ℓ ranges from 3 to 5 mm. As porosity increases from essentially zero to about 20%, a decrease in the modeling dimension could be considered, although it was not done in this work. For all three densities studied, the slab half-thickness was used for the diffusion pathlength for self-consistency, resulting in D_{eff} .

As can be seen from Fig. 2, the D_{eff} determined from this study are consistent in terms of activation energy with those determined by Jones and Gibson [8], and by Abramov [9] from permeation tests on unirradiated Be. The orders of magnitude are also consistent with each other as well as other data on hydrogen-isotope diffusion in metals. The results of Kawamura [10], however, show an activation energy much higher and more typical of metal oxides (e.g., BeO). The magnitude is also much lower than the current study in the temperature range of interest.

Tritium release from and retention in Be appear to be governed by more than one mechanism, i.e., either diffusion, surface desorption, or some combination of these two, as well as some trapping mechanism. The residual ^3H in the sample after annealing at a particular temperature suggests that ^3H is "trapped" either by impurities (e.g., BeO) or by irradiation-induced defects (e.g., He atoms or bubbles). Macauley-Newcombe [5] and Swansiger [6] describe the importance of the BeO layer in any permeation or diffusion measurement of Be. During post-irradiation annealing, there may be a time dependence to the detrapping of ^3H before it is available for diffusion through the bulk and desorption from the surface. Aside from the probable time dependence of detrapping, other parameters that may change during an anneal are He distribution (e.g., atoms changing to individual bubbles changing to interlinked bubbles) and thickness of internal and surface BeO layers. More work needs to be done in these areas to quantify these mechanisms and effects.

The nondiffusional ^3H burst release, first predicted [7] in 1985 to occur at about 923 K due to the migration of He bubbles to form interconnected grain-edge tunnels to the surface, has been observed in all these materials, and was first described in [1]. Accumulated evidence includes 1) release-peak widths, 2) nearly complete loss of remaining ^3H inventory, 3) before and after SEM photographs showing extensive restructuring and void creation, and 4) time lag of release burst. The observed burst release temperature (873 to 1173 K) and observed time lag (2 to 4 h) appear to be sensitive to density, He content, and irradiation temperature. In contrast to the 873 K burst releases seen for the low-He content 81% TD and high-He content 100% TD Be, the low-He content 99% TD Be showed only 10% of the ^3H inventory had been released by 873 K. In this case, the temperature was increased until a ^3H burst release occurred at 1173 K, releasing the remaining inventory of over 50% of the total. Surprisingly, the residual He after the burst release from the 81% TD material was measured at 91% of original inventory. This high residual level of He apparently indicates that although the ^3H burst release may be caused by He bubble coalescence and void expansion, very little He actually escaped.

5. Conclusions

Tritium release measurements and data analysis on three densities of low-irradiation temperature Be have been completed and compared. A clear trend of increased ^3H release with lower density is seen. After long-time at 773 K, the low-density Be released 89% of the ^3H inventory, while the higher density Be materials released only 0.6 to 3.3%. The He generation rate for this Be was found to range from 3350 to 5300 appm/ 10^{22} n/cm².

The effective ^3H diffusivities for the Be materials studied in the present work, and also from new data analysis of the earlier described fully dense material, were found to be

$$81\% \text{ TD Be: } 1.7 \times 10^{-11} \exp(-3.5 \text{ kJ/mol/RT})$$

$$99\% \text{ TD Be: } 1.6 \times 10^{-10} \exp(-9.5 \text{ kJ/mol/RT})$$

$$100\% \text{ TD Be: } 1.4 \times 10^{-10} \exp(-11.5 \text{ kJ/mol/RT})$$

Tritium release data for both the 81% TD and the 99% TD sample were matched reasonably well by the diffusion/desorption model. The model provides evidence for a changing mechanism over both temperature and density, but indicates that diffusion is the primary mechanism with a small and changing contribution from surface desorption. Future work will focus on the mechanism of ^3H trapping in Be and the time dependence of detrapping as a function of temperature.

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Table 1: Fabrication and Irradiation Parameters

Parameter	81% TD	99% TD	100% TD
Fabrication Method ⁽¹⁾	CIP then 1323 K - 4 h	CIP then 1523 K - 4 h	HIP until fully dense
Neutron Fluence (n/cm ² , >1 MeV)	2.6×10^{21} ($\pm 0.2 \times 10^{21}$)	2.6×10^{21} ($\pm 0.2 \times 10^{21}$)	5.0×10^{22} ($\pm 0.3 \times 10^{22}$)
Irradiation Temp.	≈348 K	≈348 K	≈348 K
Target Density	80% TD	97% TD	100% TD
Measured Density ⁽²⁾	80.9%	99.6%	100%
BeO	0.9 wt%	0.9 wt%	1.7 wt%
Grain size	25 u	25 u	10-40 u
Estimated swelling	0.1%	0.1%	2-3%

Notes:

(1) Fabrication Methods:

81% TD: Cold isostatically pressed, then sintered at 1323 K for 4 h.

99% TD: Cold isostatically pressed, then sintered at 1523 K for 4 h.

100% TD: Hot isostatically pressed to full density.

(2) Densities of 80.9% and 99.6% TD samples were determined at Rocky Flats after fabrication by dimension and weight measurements.

Table 2: Tritium and Helium Assay and Release Characteristics

Parameter		81% TD	99% TD	100% TD
³ H Assay (pre-anneal)		6600 MBq/g	8570 MBq/g	302000 MBq/g
		55.3 appm	71.8 appm	2530 appm
⁴ He Assay (pre-anneal)		1.82 cm ³ STP/g	2.17 cm ³ STP/g	65.0 cm ³ STP/g
		733 appm	872 appm	26100 appm ⁽³⁾
He Generation Rate (appm/10 ²² n/cm ²)		2820	3350	5300 ±300
³ H Fractional Release (%) at Temperature:	573 K ⁽²⁾	3.2	0.10	0.01
	673 K	38	0.55	0.25
	773 K	89	3.3	0.6
	873 K	99 ⁽⁴⁾	9.7	90 ⁽⁴⁾
	973 K	(1)	26.4	(1)
	1073 K	(1)	33.2	(1)
	1173 K	(1)	96.5 ⁽⁴⁾	(1)
³ H Retention (post-anneal)		1.4%	(1)	10%
He Retention (post-anneal)		91.7%	(1)	(1)
Sample Weight		0.353 g	0.112 g	0.473 g
Sample Thickness		5.25 mm	4.50 mm	3.2 mm
³ H Content in Sample		2330 MBq	960 MBq	143000 MBq

Notes:

- (1) not measured.
- (2) Actual release temperatures of 100% TD test: 573, 684, 784, 884 K.
- (3) The value of 26100 appm He for the 100% TD Be is a revised value from earlier published data [1] and based on new measurements. This revised value is due to improvements in the analytical method for measuring retained He [11].
- (4) Burst release of ³H observed.

Table 3: Summary of Tritium Diffusivity and Desorption Rate Constant

Be Density	Time Regime	Diffusivity, D_{eff} (m^2/s)	Surface Desorption Rate Constant, k_{eff} (m/s)
81% TD	$50 < t < 150$ h	$1.7 \times 10^{-11} \exp(-3.5 \text{ kJ/mol/RT})$	$8.8 \times 10^{-5} \exp(-18 \text{ kJ/mol/RT})$
99% TD	$25 < t < 400$ h	$1.6 \times 10^{-10} \exp(-9.5 \pm 3.0 \text{ kJ/mol/RT})$	$4.8 \times 10^{-8} \exp(-4.6 \text{ kJ/mol/RT})$
100% TD	$1 < t < 25$ h	$1.4 \times 10^{-10} \exp(-11.5 \text{ kJ/mol/RT})$

Figure 1: Stepped-Anneal tritium release curves for 81% TD Be from 573 to 873 K, and for 99% TD Be from 573 to 1173 K, showing tritium release fraction versus time in h. 100% TD Be curve is found in [1].

Figure 2: Tritium diffusion coefficients for Be from the present study and from the literature.

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