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GAS RETENTION IN IRRADIATED BERYLLIUM

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ABSTRACT

Helium (an inert gas) with low solubility in beryllium is trapped in irradiated beryllium at low temperatures ($<100^{\circ}\text{C}$) while the tritium generated may have some mobility and be released. The subject of tritium retention in irradiated beryllium within fusion reactor blankets is of considerable interest in their conceptual design. Results from experiments on three sets of irradiated beryllium specimens are examined in this paper. The beryllium specimens were irradiated at about 75°C in capsules to protect them from the cooling water. One set of samples was irradiated to $\sim 3 \times 10^{22} \text{ n/cm}^2$ ($E > 1\text{MeV}$). In these samples the calculated helium generated was $\sim 14,100 \text{ appm}$. They are described in terms of swelling, annealing, microstructure, and helium bubble behavior (size, density and mobility). A second sample was irradiated to $\sim 5 \times 10^{22} \text{ n/cm}^2$ ($E > 1\text{MeV}$). In that one the calculated helium and tritium generated were $\sim 24,000 \text{ appm He}$ and $\sim 3,270 \text{ appm}$, and tritium content was examined in a dissolution experiment. After decay for 8.2 years assuming 100% retention the tritium content was estimated to be $\sim 2,100 \text{ appm tritium}$ ($\sim 32.6 \text{ Ci}$) in 4.7-g samples. The total tritium measured was 32.79 Ci. Most of the tritium was released as gas to the glovebox indicating the generated tritium was retained in the helium bubbles. In a third set of experiments a specimen was examined by annealing at a succession of temperatures to more than 600°C for tritium release. In the temperature range of $300\text{-}500^{\circ}\text{C}$ little release (0.01 - 0.4%) occurred, but there was a massive release at just over 600°C . The results of these experiments indicate that the tritium tends to collect in the small helium bubbles which have low mobility at temperatures less than 500°C . Theories of swelling appear to adequately describe bubble behavior with breakaway release occurring at high helium contents and at large bubble diameters.

GAS RETENTION IN IRRADIATED BERYLLIUM

INTRODUCTION

Gas retention in nuclear fuels and neutron irradiated metals, especially beryllium, has been of considerable interest for some time.⁽¹⁻⁴⁾ Recently, the subject of tritium retention in the beryllium of breeding blankets has been attracting attention in fusion reactor safety analyses. Although much information is available on the behavior of helium in beryllium, little attention has been given to the accompanying tritium in beryllium. Since helium (an inert gas) is considered to have very low solubility in beryllium, while tritium may have appreciable solubility, the question arises as to whether the tritium follows the helium into small bubbles and behaves as does the helium gas.

Results from three sets of irradiated beryllium specimens are examined in this analysis. The beryllium specimens were all irradiated as part of the Advanced Test Reactor (ATR) surveillance program. Samples were nominally 1 cm in diameter and 3 cm long with a mass of about 4.7 g.

The beryllium specimens were irradiated in the Experimental Test Reactor (ETR) and ATR in capsules at about 75°C to protect them from the cooling water. The solid chemistry of the hot-pressed, beryllium specimens is given in Table I. These specimens had a structure of equiaxed grains with fine oxide particles at the grain boundaries and through the grains. The metallic impurities which exceed the solubility limit are finely dispersed, primarily along grain boundaries. The average grain diameter was about 25 μm .

SWELLING, ANNEALING, AND TEM RESULTS

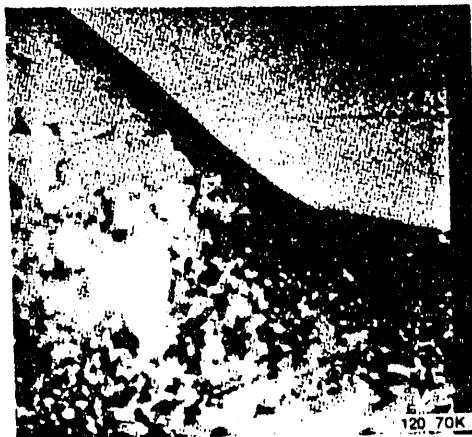
The first set of experiments to be discussed includes four specimens from which density, annealing at three temperatures, and transmission electron microscopy (TEM) measurements were obtained. The helium generated during irradiation in the beryllium is highly insoluble and would precipitate as very fine bubbles except that re-solution of the gas (because of displacement) and

Table 1. Solid Chemistry of Hot-Pressed Beryllium.

Element	Lot 2811 Content %	Lot 2870 Content %
Be	98.67	98.26
BeO	1.67	1.70
C	0.110	0.100
Al	0.100	0.085
Cr	0.011	0.010
Fe	0.130	0.153
Mg	0.004	0.006
Mn	0.016	0.012
Ni	0.014	0.014
Cu	0.009	0.008
Si	0.030	0.030
Ti	0.024	0.021

transmutation reactions keep the structure "stirred up" at this irradiation temperature (< 100°C). This effect is evidenced by TEM pictures of specimens cut from samples after irradiation (shown in Figure 1). Four irradiated specimens were cut in half; one half was used for the preanneal control for density and TEM, the other half was annealed at temperatures between 200 and 500°C for one hour. The results of the density measurements are given in Table 2 and Figure 2. From the electron microscopy (Figures 1 and 3) it can be seen that the swelling can be correlated with the resolution of gas bubbles. At temperatures < 100°C after irradiation, and after a 200°C, one-hour annealing, the gas bubbles are not resolved. After annealing at 300, 400, and 500°C, the gas bubbles are resolved at about 30, 60, and 90 Å.

Inasmuch as the tritium may follow the helium into the bubbles, some insight into the probable tritium release behavior can be ascertained from the beryllium swelling, TEM results, and theories of bubble behavior.⁽¹⁻⁴⁾



A. Specimen 120, Fluence of
 $3.1 \times 10^{22} \text{ n/cm}^2$ at $T = -100^\circ\text{C}$.



B. Specimen 169-A, Fluence of
 $3.0 \times 10^{22} \text{ n/cm}^2$ at $T = -100^\circ\text{C}$.



C. Specimen 169-B, Fluence of $3.0 \times 10^{22} \text{ n/cm}^2$ at $T = 200^\circ\text{C}$ for one hour.

Figure 1. Bubbles not resolved.

Assuming uniform bubble size, the number of bubbles/cm³, η , can be calculated from the swelling. Beginning with the $\Delta\rho/\rho$ (%) values given in Table 2, the change in specific volume is given by

Table 2. Density Measurements

Spec. No.	Annealing Temp. (°C)	$(E > 1 \text{ MeV}) \times 10^{22}$	Density (g/cm ³)	Irradiated		Annealed Density (g/cm ³)	Density Change After Annealing	Density Change After Irradiation	$-\Delta\rho/\rho(\%)$
				Preirradiated	Preannealed				
169	200	3.024	1.8508	1.8222	1.8223	1.55	1.54		
172	300	3.192	1.8512	1.8235	1.8206	1.50	1.65		
175	400	3.325	1.8511	1.8209	1.7914	1.63	3.23		
21	500	3.441	1.8523	1.8260	1.7507	1.42	5.49		

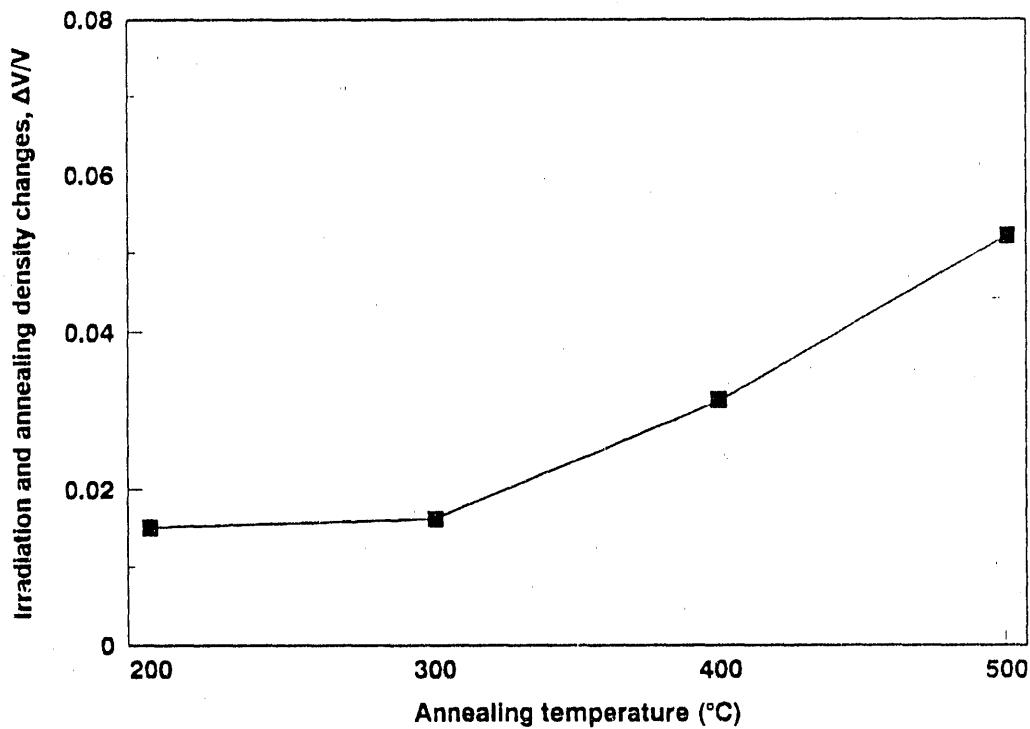


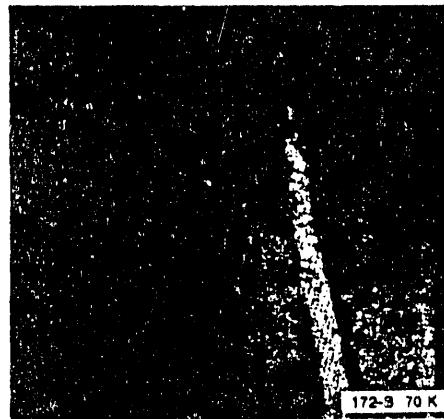
Figure 2. Irradiation and annealing density change.

$$\frac{\Delta V}{V} = \frac{-\frac{\Delta \rho}{\rho} (\%)}{100 + \frac{\Delta \rho}{\rho} (\%)} \quad (1)$$

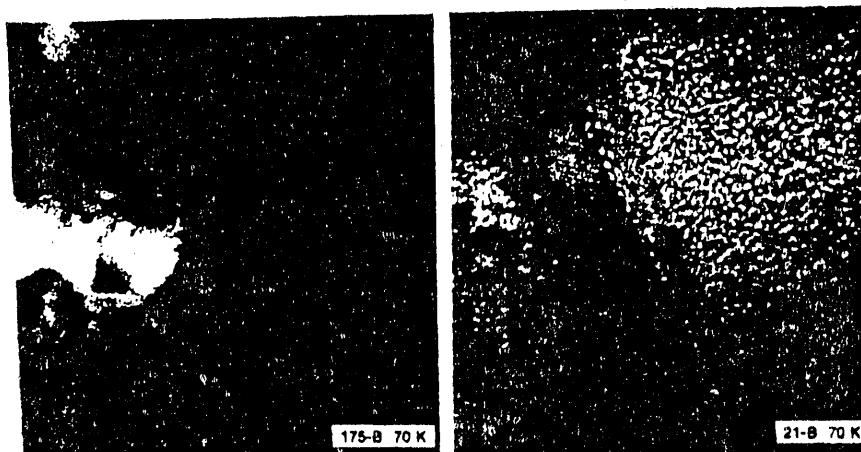
and then

$$\eta = \frac{3}{4\pi r^3} \frac{\Delta V}{V} \left(\frac{\text{bubbles}}{\text{cm}^3} \right) \quad (2)$$

η is calculated using the radii from Figure 3 for the samples annealed at 300, 400, and 500 °C, as 1.5×10^{17} , 3.7×10^{16} , and 1.9×10^{16} bubbles/cm³, respectively. The partial pressure of He in these bubbles can be estimated from the number of He atoms assumed to be in the bubbles and the temperature. It is given by



A. Specimen 172-B, Fluence of 3.2×10^{22} n/cm² at T = 300 °C for one hour. Bubbles about 30 Angstroms diameter.



B. Specimen 175-B, Fluence of 3.3×10^{22} n/cm² at T = 400 °C for one hour. Bubbles about 60 Å diameter. C. Specimen 21, Fluence of 3.4×10^{22} n/cm² at T = 500 °C. Bubbles about 90 Å diameter.

Figure 3. Bubbles resolved after annealing at the temperatures indicated.

$$P_{\text{He}} = \frac{n_g V}{\Delta V} kT \quad (3)$$

where n_g is the number of He atoms generated per cubic meter based on neutron cross sections and fluence. Assuming a generation rate of 0.0047 atoms He/atom Be/ 10^{22} n/cm² ($E > 1$ MeV), n_g is estimated to be 1.86×10^{27} , 1.94×10^{27} , and 2.00×10^{27} atom He/m³ Be for the specimens at 300, 400, and 500 °C, respectively. Using the ideal gas law, partial pressures are calculated to be 875, 540, and 369

MPa, respectively. These values suggest the ideal gas law only applies poorly as will be indicated later.

The radii estimated based on the TEM images of Figure 3 (30, 60, and 90 Å) may be compared with those calculated using the perfect gas law and the relationship:

$$r = \frac{2\gamma \frac{\Delta V}{V}}{n_g kT} \quad (4)$$

where:

$$n_g = \text{number of gas atoms/m}^3$$
$$\gamma = \text{surface energy } (\sim \text{ J/m}^2),$$

Values so calculated were 23, 37, and 54 Å, in reasonable agreement with those estimated from TEM.

The bubbles will migrate because of the annealing temperature gradient (dT/dx), and the velocity of the bubbles will depend on the surface and volume diffusion coefficients,⁽³⁾ as well as the concentration gradients. The self-diffusion coefficient for beryllium,⁽⁵⁾

$$D = 5.2 \times 10^{-5} \exp \left[-\frac{18922}{T \text{ (K)}} \right] \left(\frac{\text{m}^2}{\text{s}} \right), \quad (5)$$

is small ($< 2 \times 10^{-14} \text{ m}^2/\text{s}$) at these temperatures (200-600°C), and since helium (an inert gas) is practically insoluble in beryllium, the diffusion coefficient for tritium will be used to estimate the bubble mobility. The diffusion coefficient for tritium in beryllium given by Jones and Gibson⁽⁶⁾ is:

$$D = 3 \times 10^{-11} \exp \left[-\frac{2222.4}{T \text{ (K)}} \right] \left(\frac{m^2}{s} \right) \quad (6)$$

This coefficient will be used in the equation to estimate the velocity of the bubbles (V_s), from which the distance the bubbles travel during a one-hour annealing can be calculated:

$$V_s = \frac{36}{\pi^2} \frac{\Omega^{1/3}}{r} \frac{D}{T} \frac{dT}{dx} \quad (7)$$

where:

Ω = atomic volume of Be ($8.11 \times 10^{-30} \text{ m}^3/\text{atom}$)

$\frac{dT}{dx}$ = $100^\circ\text{C}/\text{m}$ (calculated by thermal analysis for specimens placed in a furnace for one hour annealings)

As shown in Figure 4, the bubble diameter at 600°C is obtained from an extrapolation. The calculation for V_s at 300, 400, 500, and 600°C gives 5.28×10^{-14} , 4.02×10^{-14} , 3.56×10^{-14} , $3.28 \times 10^{-14} \text{ m/s}$, respectively, and gives a total distance of $5.8 \times 10^{-10} \text{ m}$ for one-hour annealings. Since the grain diameter is approximately $25 \mu\text{m}$, the fraction of the grain diameter travelled in the one-hour annealings is 2.4×10^{-5} . Thus, the bubbles travel a very short distance in the grains for the one-hour annealings.

If the bubbles are randomly oriented within the grain, they will touch each other and the gas will be released⁽³⁾ when the radius (r) is given by:

$$r = \frac{2\gamma}{3kTn_g} \quad (8)$$

where:

n_g = the number of gas atoms/ m^3 in the grain ($\sim 2 \times 10^{27} \text{ atoms}/\text{m}^3$).

Thus, at 500°C , the effective bubble radius may be estimated as

$$r = \frac{2}{3(1.38 \times 10^{-23})(773)(2 \times 10^{27})} = 312 \text{ \AA} \quad (9)$$

The behavior of the helium (and trapped tritium) for the set of annealed specimens has been described in terms of theories of swelling and gas retention. The calculations for annealing up to 500°C, using the perfect gas law, indicate that the bubbles need to grow larger before "breakaway" release of the gas occurs (the swelling at which a large number of bubbles touch, releasing their gas content). For the specimens irradiated to $3 \times 10^{22} \text{ n/cm}^2$ (gas content of $2 \times 10^{21} \text{ atom He/cm}^3$ beryllium), a radius of 312 Å was indicated as needed for gas release. However, since tritium is not insoluble in beryllium, as is the inert gas helium, it may be that some tritium would be released at temperatures less than 500°C. There is a limit to the amount of gas which can be contained within

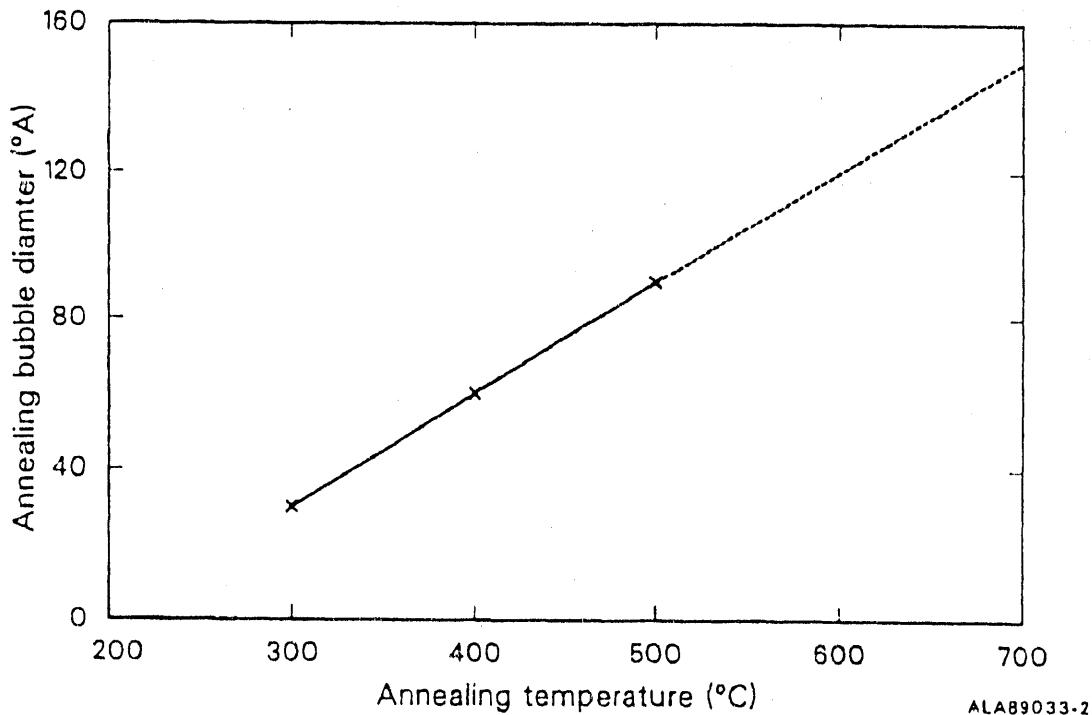


Figure 4. Annealing bubble diameter vs temperature.

the grains. At the small bubble radius a better gas law (Van der Waal's) has been used. Barnes and Nelson⁽³⁾ have made this correction using Van der Waal's law and have shown the concentration limit for "breakaway" swelling, at the small bubble radii, to be at approximately 3×10^{27} gas atoms/m³ (Figure 5). The maximum amount of gas that can be contained within the grains (mg) is plotted as a function of radius for 500°C and 1,750°C. Thus, as indicated in Figure 5, "breakaway" swelling would be expected for specimens irradiated to 5×10^{22} n/cm² ($E > 1$ MeV), ($\sim 3 \times 10^{27}$ atoms He/m³ Be) at temperatures of 600°C.

DISSOLUTION EXPERIMENT

The second set of experiments discussed utilized one specimen that had been irradiated to a fluence of 5×10^{22} n/cm² ($E > 1$ MeV). The specimen was examined at Sandia National Laboratory, Livermore. The beryllium specimen, with the same composition as the samples in the first set of experiments discussed and original dimensions of 1.02-cm diameter x 3.12-cm long with a mass of 4.70 g, had been irradiated to high fluence with resulting calculated high helium and tritium contents ($\sim 24,000$ appm He or 3×10^{21} atoms He/cm³, $\sim 3,270$ appm tritium). This specimen was analyzed for tritium in a dissolution experiment. Since it had been decaying for 8.2 years before being analyzed, the tritium content, assuming 100% retention, was expected to be $\sim 2,100$ appm tritium (~ 32.6 Ci).

The dissolution experiment was performed in a glovebox located in the Tritium Research Laboratory of Sandia National Laboratories in Livermore, CA. The sample was dissolved in a series of four steps using 100 mL of 3-molar sulfuric acid in each step. The process time for each dissolution was approximately 10 minutes. After the dissolution was completed, 25 mL samples of each etch solution were collected for scintillation counting. This produced scintillation samples with a tritium signal too intense for counting. These samples were diluted by a factor of 20 to obtain samples that could be counted without serious deadtime losses on the detector. While the beryllium sample was being dissolved, an ionization detector inside the glovebox measured the amount of tritium not being collected in the acid solutions. The glovebox was isolated during the operation. Results are shown in Table 3.

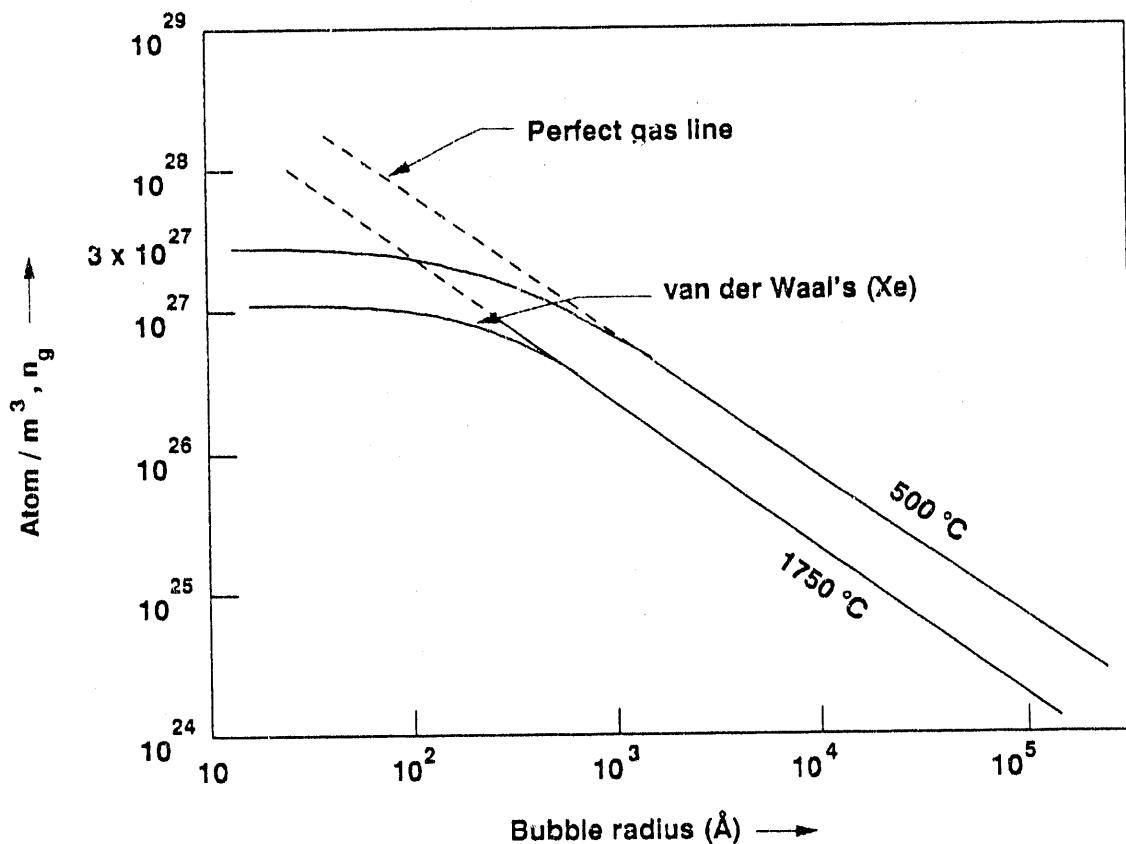


Figure 5. Breakaway Swelling. The maximum amount of gas which can be contained within the grains (n_g) as a function of radius for 500°C and 1750 °C.

There was a small decrease in tritium concentration as the layers were removed. Concentrations were measured at approximately 7.3 Ci/g at the outside of the sample and about 6.2 Ci/g near the center. The most surprising result of the experiment was the failure of the acid solution to capture the released tritium. Typically, when tritium containing materials are dissolved in acid solutions, the tritium isotopically exchanges with hydrogen in the solution and is retained. This did not happen in this experiment. One possible explanation is that the tritium in the beryllium was in the form of tritium molecules (tritium and helium in the bubbles).

Table 2. Tritium Dissolution Experiment Results.

Amount of Sample Removed (g)	T in Acid (Ci)	T in Glovebox (Ci)
1.35	0.22	9.8
1.10	0.20	7.8
0.85	0.15	5.4
1.45	0.22	9.0
	0.79	32.0

It should also be noted that the dissolved beryllium specimen apparently contained nearly all the tritium generated (minus that which decayed). Diffusion of tritium from the beryllium at temperatures less than 100°C is minimal. The experimental results suggest tritium follows the helium into small bubbles. As shown in Figure 1 (TEM photographs for the other specimens), the bubbles could have been present, but not resolved because of the tangled structure from irradiation. At temperatures sufficient to anneal the irradiation damage (interstitial beryllium atoms), the bubbles became resolved (as shown in the TEM photographs).

ISOTHERMAL ANNEALING - HELIUM RELEASE

The third set of experiments involved irradiated specimens sent to Dr. David Baldwin⁽⁷⁾ at Battelle Northwest for tritium release measurements. These specimens were also of the same composition. They, too, were irradiated to 5×10^{22} n/cm² ($E > 1$ MeV) and contained 24,000 - 30,000 appm Helium. It is sufficient for the present purpose to state that Dr. Baldwin's experiment consisted of heating a sample in stages (300, 411, 511, and 611°C). There was modest release of tritium at the lower temperatures, but a massive release of the tritium was observed at 611°C.

DISCUSSION

Billone⁽⁸⁾ has reviewed Balwin's data and indicated that the recent tritium release data from irradiated Be in the temperature range of 300-500°C gives little (0.01-0.4%) release; however, a massive release occurs at approximately 600°C. Within the assumptions in the calculations, we have shown that upon annealing, helium in beryllium and, presumably, tritium does produce bubble sizes as theories⁽¹⁻⁴⁾ would indicate in the 300-500°C temperature range. The helium (Figures 1 and 3) and tritium (as shown in the dissolution experiment) did seem to be retained as if in bubbles. The bubbles gave the appearance of slow growth as a function of annealing temperature, even at temperatures of 300-500°C. However, in annealing tests at those temperatures, the distance traversed was less than a grain diameter, even after 100 hours. The bubbles may have been affected by pinning from oxide and impurity particles, and the temperature gradients certainly did not persist for 100 hours during annealing tests.

There will be some re-solution of the gas during irradiation because of displacement and transmutation reactions. Figure 6 (taken from Billone⁽⁸⁾) depicts the fraction of "trapped" hydrogen isotope in Be as a function of annealing temperatures. Billone showed (Figure 6) an apparent anomaly between 500 and 600°C in the tritium release for the irradiated beryllium; however, the helium content of the specimens irradiated to 5×10^{22} n/cm² (gas content of 3×10^{27} atoms/m³) was at the limit for breakaway release of the helium, even at the small bubble diameter of 120 Å (Figure 5). The anomaly was apparently due to the breakaway release of helium.

CONCLUSIONS

Most of the tritium in irradiated beryllium evidently follows the helium into small bubbles at irradiation temperatures of < 100°C and stays in the bubbles for a long time (> 8.2 years).

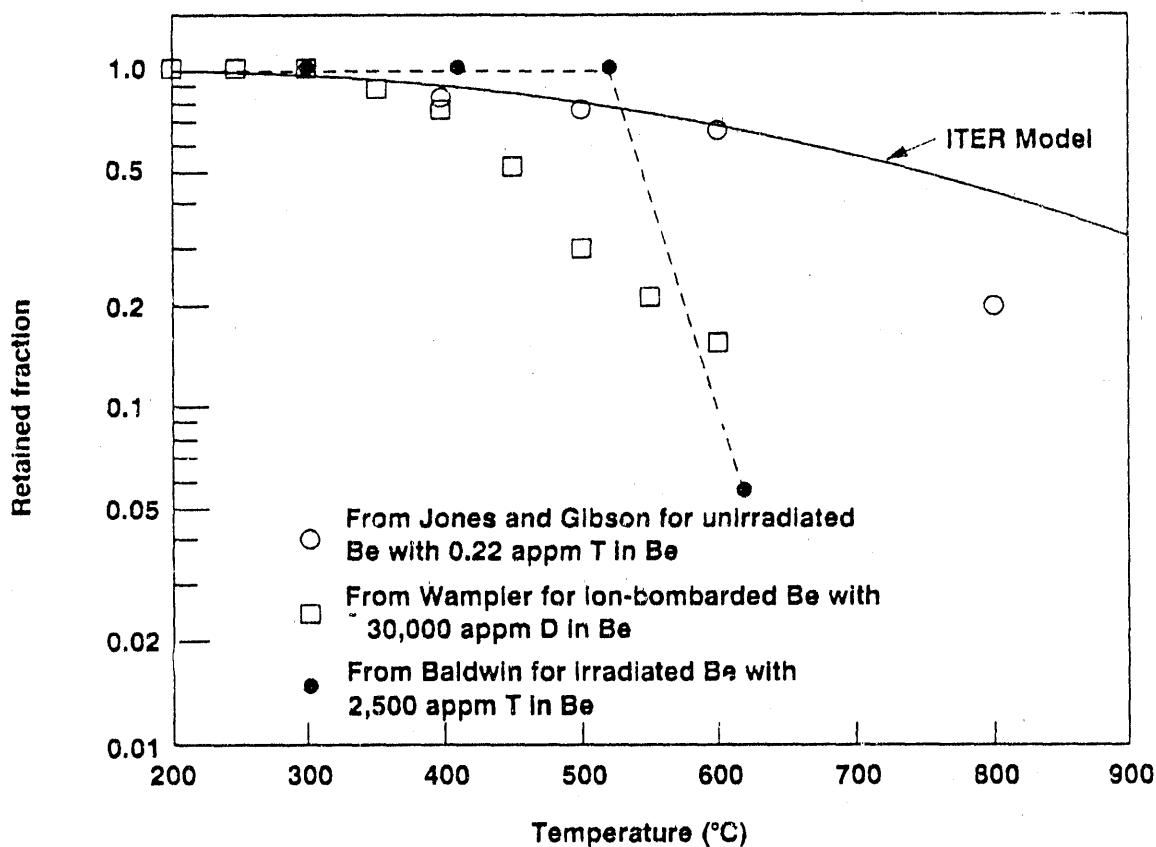


Figure 6. Breakaway swelling. The maximum amount of gas which can be contained within the grams (mg) plotted as a function of radius for 500 and 1750 °C.

The behavior of the bubbles containing the helium and tritium in annealing experiments can be described in terms of the theories of bubble behavior.

The massive release of helium and tritium that occurs at 600°C can be described in terms of breakaway release of the gas in bubbles that occurs because of the limit of gas content in the beryllium structure at high gas contents.

Release of helium from irradiated beryllium at gas concentrations less than the breakaway limit may occur in accordance with theories of swelling and gas retention. The tritium release apparently follows the helium at intermediate temperatures.

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