Stepped-Anneal and Total Helium/Hydrogen Measurements in High-Energy Proton-Irradiated Tungsten


Abstract: To provide structural material design data for the Accelerator Production of Tritium (APT) project, a 1 mA, 800 MeV proton beam at the Los Alamos Neutron Science Center (LANSCE) was used to irradiate a large number of metal samples, including a tungsten target similar to that being considered as the neutron source for the tritium production. The maximum proton fluence to the tungsten target was \(-10^{21}\) protons/cm\(^2\). An unavoidable byproduct of spallation reactions is the formation of large amounts of hydrogen and helium. Postulated accident scenarios for APT involving the use of tungsten rods clad with Alloy 718, raise concerns as to the amount and rate of release of these gases due to temperatures increases from afterheat accumulation, with the major concern being pressurizing and possibly failure of the cladding. To address these issues, portions of the LANSCE tungsten rods were subjected to temperature histories calculated as likely to occur, and the time-dependent evolution of helium and hydrogen gases was measured.

Stepped-anneal and total helium/hydrogen measurements were conducted on multiple samples of the tungsten material. Helium measurements were conducted at Pacific Northwest National Laboratory (PNNL) using a high-sensitivity magnetic-sector isotope-dilution helium analysis system. Stepped-anneal measurements were conducted at temperatures from \(-25^\circ\text{C}\) to \(-1600^\circ\text{C}\) in \(-100^\circ\text{C}\) steps. Total helium measurements were conducted by rapid vaporization after completion of the stepped-anneal process, and are compared with Monte Carlo calculations performed at Los Alamos National Laboratory (LANL) using the LAHET code system.

Hydrogen measurements were conducted between \(-750^\circ\text{C}\) and \(-1200^\circ\text{C}\) using a high-temperature furnace that had been extensively modified for the application. Hydrogen detection was accomplished by periodic sampling of the furnace gas using a separate quadrupole analyzer. Hydrogen measurements are also compared with LANL calculations.

Keywords: helium measurements, hydrogen measurements, APT, Accelerator Production of Tritium, hydrogen release, helium release, tungsten targets, Alloy 718
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Introduction

The Accelerator Production of Tritium (APT) project [1] has been proposed as a solution to the national need for tritium. One key technical issue that must be addressed by APT is radiation damage to materials in the mixed high-energy proton and neutron environment. To address this issue, a materials irradiation program [2] using the 800-MeV proton accelerator at the Los Alamos Neutron Science Center (LANSCE) has been initiated. To simulate the tungsten neutron source in the APT target, a series of tungsten rods were placed in the LANSCE materials irradiation.

While reviewing postulated accident scenarios for the APT target, the question of gas build-up inside the Alloy 718 clad tungsten rods was raised. Spallation reactions typically result in copious amounts of helium and hydrogen being produced in the target material. If enough gas is produced and released from the target material, and then trapped at the tungsten/cladding interface, this gas could result in the failure of the target-cladding if pressure buildup occurred. For the materials irradiation at LANSCE, sufficient room was allowed to accommodate any released gas. However, for the APT target design, this option may not be satisfactory. The tungsten rods in the LANSCE materials irradiation were used to address two important questions: 1) is the produced gas released from the target material and at what rate, and 2) how accurately can gas production be predicted for the APT target.

Tungsten Analysis Samples

Five tungsten samples were prepared at Los Alamos National Laboratory (LANL) for the helium and hydrogen measurements. Each sample was in the form of a thin disk cut from a 3.18 mm diameter tungsten target rod that had been irradiated with 800 MeV protons to a fluence of about 10^{21}/cm^{2}. As the rods were highly radioactive, sample preparation was done in a hot cell. Extensive radiometric analysis was conducted on the samples to provide data for comparison with model calculations discussed below.

Helium Measurements

Helium Analysis System

Helium analyses were conducted by gas mass spectrometry at Pacific Northwest National Laboratory (PNNL). Details on the mass spectrometry system used have been presented elsewhere [3,4]. Helium contents were determined by heating and/or vaporizing each sample in a resistance-heated crucible in one of the mass spectrometer system's high-temperature vacuum furnaces. Helium values were determined either by direct measurements of the mass spectrometer helium signal, or by an isotope-dilution technique where the released helium is compared with a known quantity of added $^3$He "spike". The helium spikes were obtained by expanding and partitioning known quantities of gas through a succession of calibrated volumes integrated into the analysis system. The mass spectrometer was calibrated for mass sensitivity during each series of runs by analyzing known mixtures of $^3$He and $^4$He. Mass discrimination values for the system typically averaged about 1.5. Reproducibility of the analysis system for samples with known homogeneous helium content is ~0.5%. Absolute accuracy is better than 1%.
Stepped-Anneal and Total Helium Measurements

For the helium measurements, small specimens were cut from each tungsten disk using small diagonal wire cutters. Two of these specimens were then analyzed for both stepped-anneal helium release and then later for total helium by rapid vaporization. The mass of each analyzed specimen was determined using a microbalance with calibration traceable to the National Institute of Standards and Technology (NIST). Mass uncertainty is conservatively estimated to be ±0.002 mg.

For the stepped-anneal helium release measurements, the specimens were individually loaded into the central section of one of the analysis system's standard 0.48 cm diameter graphite crucibles. Small graphite plugs were placed at each end of the hole to position the samples as close as possible to the middle of the crucible. A diagram of the setup, showing a section of the high temperature furnace used, is shown in Figure 1.

Because of voltage isolation problems encountered with the thermocouple, crucible temperature was measured using an optical pyrometer. Temperature values below the usable range of the pyrometer (<750°C) were determined by applying a linear correction to the thermocouple data based on earlier thermocouple/pyrometer intercomparisons. The temperature range for sample W-2 ranged from -25°C to 1600°C in -133°C increments. Temperature range for sample W-3 ranged from -25°C to 1200°C in -100°C increments. Except for the final temperature step, each step was held for a period of 10 minutes, with helium measurements being made at the approximate midpoint of each interval. For the final (highest) temperature, multiple measurement were taken in approximately 5-minute intervals. The time to reach equilibrium for each temperature was approximately 1 minute. Temperature uncertainty is estimated to be ±50°C. As both 3He and 4He were expected in the samples, no 3He spike was used.

Results of the stepped-anneal measurements are shown graphically in Figure 2 and Figure 3. Helium results are plotted in atomic parts per million (appm), based on a calculated value of 0.3276 x 10^22 atoms per gram. Helium levels were corrected for background helium buildup in the analysis furnace as a function of time, obtained from separate “control” analyses conducted immediately after the sample runs. Background levels increased approximately linearly with time for both helium isotopes, and were in the range of 10^12 atoms for 3He and 10^13 atoms for 4He. The estimated uncertainty in the stepped-anneal results is ±10^17 atoms (±0.1 appm), and is dominated largely by variability in the helium background.

For sample W-2, helium release is first observed at a temperature of ~800°C. From 800°C up to the final temperature of ~1600°C, the incremental helium release is approximately the same for each temperature step, although there is some indication of an slowly increasing release rate up to ~1400°C. At the final temperature of 1600°C, a total of five measurements were made, and these data show a leveling off of the gas release at a value of ~1.4 appm. Similar trends were observed for sample W-3, with the 4He released tending asymptotically to ~1.0 appm at the highest temperature of ~1200°C. For this second sample, however, there is little evidence for an increasing helium release rate with temperature (above ~800°C). The 3He release for both was at or below the detection limit of the analysis system (~10^12 atoms) for the particular setup used in these tests. Variability in the helium release curves is due largely to variability in the subtracted helium background as discussed above.

Following the stepped-anneal measurements, the two tungsten specimens were relocated, in their original crucibles, to different positions in the same furnace for subsequent vaporization analysis. For these measurements, the residual helium contained in the specimens was determined using the isotope-dilution method. Prior to the addition
of the spike, however, a first aliquot of the sample gas was taken for a determination of the helium isotopic ratio in the sample itself.

Total helium measurements in the two samples after vaporization are given in Table 1. Total helium measured was 752 appm for W-2 and 713 appm for W-3, with an average of 733 ± 28 (1σ) appm. The $^4\text{He}/^3\text{He}$ isotopic ratio observed in the two specimens was 13.9 and 13.7, respectively, with an average value of 13.8 ± 0.1 (1σ). Background levels for the total helium measurements were negligible compared with the atoms measured. The absolute uncertainty (1σ) in the helium contents is estimated to be approximately 1% to 2%.

![Figure 1 - Stepped-Anneal Helium Release Setup](image-url)
Figure 2 - Helium Release in Sample W-2

Figure 3 - Helium Release in Sample W-3
As can be seen from Figure 2 and Figure 3, and Table 1, helium release from the tungsten during the initial stepped-anneal tests was small compared to the total helium inventory. For W-2, the total $^4\text{He}$ released at 1600°C was only $\sim 0.2\%$ of the total $^4\text{He}$. Similarly, for W-3, the $^4\text{He}$ released by 1200°C was only $\sim 0.1\%$ of the total.

**Hydrogen Measurements**

*Hydrogen Analysis System*

Hydrogen measurements were accomplished using one of the analysis furnaces attached to the helium analysis system that had been extensively modified for the task. A schematic diagram of the hydrogen analysis setup is shown in Figure 4. As with the total helium measurements discussed earlier, the hydrogen measurements used an isotope-dilution method with an added $^4\text{He}$ spike. Hydrogen and helium ratios were determined using a quadrupole detector attached to the helium analysis system. A liquid nitrogen-cooled U-trap was employed in the quadrupole analysis volume to reduce condensable background gas buildup. The magnetic sector instrument used for the helium measurements was not employed due to the integral use of hydrogen getters in the helium system. These getters could be bypassed by use of the quadrupole detector, but still allowed the use of other system vacuum lines and the helium spikes.

The analysis furnace consisted of a boron nitride crucible heated by a resistance-heated tungsten filament inside a water-cooled copper enclosure. The crucible temperature over the range of $\sim 750°C$ to $\sim 1200°C$ was determined using an optical pyrometer. The temperature uncertainty is estimated to be $\pm 50°C$. The inside surface of the copper was partially plated with a gold evaporation layer to minimize hydrogen uptake by the furnace walls that had been observed during initial system testing.

**Table 1 - Helium Contents in APT Tungsten Samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Material</th>
<th>Mass (mg)</th>
<th>Measured Helium (10^{14} \text{ atoms})</th>
<th>Total Helium Concentration (appm$^b$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-2</td>
<td>Tungsten</td>
<td>5.373</td>
<td>8.88 $^3\text{He}$ 123.4 $^4\text{He}$ 132.3</td>
<td>752</td>
</tr>
<tr>
<td>W-3</td>
<td>Tungsten</td>
<td>3.606</td>
<td>5.74 $^3\text{He}$ 78.50 $^4\text{He}$ 84.24</td>
<td>713</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td>733 $\pm$ 28</td>
</tr>
</tbody>
</table>

$^a$Mass uncertainty is $\pm 0.002$ mg.

$^b$Helium concentration in atomic parts per million (10$^4$ atom fraction) with respect to the total number of atoms in the specimen.
For analysis, the sample was placed in the upper stainless steel section of the furnace, and after a suitable pumping period to minimize the hydrogen background, was mechanically dropped into the heated furnace for analysis. Just prior to dropping the sample, the furnace was isolated from its vacuum pump, and the He spike was added to the enclosure. After approximately one minute, a sample of the furnace gas was taken by expanding and then trapping the gas between two valves on the analysis line. This sample was then expanded into the quadrupole analyzer volume, which at this point was also isolated from its vacuum pump. This sampling process was repeated, allowing multiple determinations of the helium/hydrogen ratio. A control run was conducted immediately prior to the sample analysis. Calibration of the quadrupole for each sample run was accomplished using a custom hydrogen/helium standard mixture attached to the analysis furnace.

**Hydrogen Release in APT Tungsten**

Hydrogen measurements were conducted on two of the irradiated tungsten samples from the original group of five samples prepared at LANL, and on two unirradiated samples received later from the same material lot. Both of the unirradiated and one of the irradiated samples were analyzed at a single temperature of ~1200°C, which is the postulated off-normal scenario for the APT project. The second irradiated sample was analyzed sequentially at four different temperatures, starting at ~750°C and increasing in ~150°C steps up to ~1200°C. The results of the hydrogen measurements are given in Table 2.

Hydrogen levels for the unirradiated materials were ~30 and ~230 appm, for an average of ~130 appm. For the irradiated tungsten sample analyzed at 1200°C, the observed hydrogen release was ~2100 appm. For each of these analyses, the observed hydrogen release for each of the three or four replicate analyses were in agreement within expected system variability. For the second irradiated sample, W-1, however, the observed releases at 750°, 900°, and 1050°C, all showed continuing hydrogen release.
Hydrogen release values for sample W-1 are also shown graphically in Figure 5. The dotted lines in the figure represent a linear extrapolation of the observed hydrogen release for each temperature for the five to six minute period that the sample was still at temperature following each set of replicate analyses. Hydrogen release rates at 750°, 900°, and 1050°C were ~60, 50, and 140 appm/min, respectively. Hydrogen release values in Figure 5 for the 1200°C step are plotted at the highest estimated total release value of ~3800 appm, however, as mentioned above, it was not possible from the available data to determine at what point in the 1050°C step the hydrogen had all been released.

Uncertainty in the hydrogen measurements is conservatively estimated at ±50%, due largely to two factors; 1) hydrogen background, and 2) hydrogen uptake by the furnace components and/or walls. Hydrogen background generally ranged from about $10^{16}$ to $10^{17}$ atoms over the time period of the analyses resulting in signal-to-noise ratios from about 1.2 to 4. Hydrogen uptake was observed in the system during system testing. Performing an in-situ gold plating of the furnace interior resulted in a significant reduction in the uptake, from maximum values of ~99% down to ~50%. This uptake is accounted for by applying a correction factor based on the C/M ratio observed for the internal helium/hydrogen standard mixture. This correction also accounts for sensitivity differences in the quadrupole analyzer for helium and hydrogen. Since the amount of hydrogen in the standard mixture is generally larger than measured in the tungsten samples, however, some uncertainty in the accuracy of this correction remains.

### Table 2 - Hydrogen Contents in APT Tungsten Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Material</th>
<th>Mass* (mg)</th>
<th>Analysis Temperature (°C)</th>
<th>Measured Hydrogen &lt;10^16 atoms</th>
<th>Measured Hydrogen (appm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-Blk-1</td>
<td>Tungsten control</td>
<td>48.8</td>
<td>1200</td>
<td>0.5</td>
<td>30</td>
</tr>
<tr>
<td>W-Blk-4</td>
<td>Tungsten control</td>
<td>87.2</td>
<td>1200</td>
<td>6.5</td>
<td>230</td>
</tr>
<tr>
<td>W-1</td>
<td>Irr. Tungsten</td>
<td>22.8</td>
<td>1200</td>
<td>160</td>
<td>2100</td>
</tr>
<tr>
<td>W-5</td>
<td>Irr. Tungsten</td>
<td>11.7</td>
<td>750</td>
<td>0.8 - 1.6</td>
<td>220 - 410</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>900</td>
<td>0.5 - 1.5</td>
<td>140 - 390</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1050</td>
<td>0.1 - 2.8</td>
<td>15 - 720</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1200</td>
<td>&lt;0.1</td>
<td>&lt;100</td>
</tr>
</tbody>
</table>

Estimated total hydrogen: 2400 - 3800

*Mass uncertainty is ±0.01 mg.

Hydrogen concentration in atomic parts per million (10^6 atom fraction) with respect to the total number of atoms in the sample.
Figure 5 – Hydrogen Release From Irradiated Tungsten at Temperatures Between 750°C and 1200°C

LAHET Calculations of Helium and Hydrogen Content

A detailed Monte Carlo model of the APT materials irradiation has been completed at LANL using the LAHET Code System (LCS) [5]. Figure 6 shows an elevation view of the Monte Carlo model with the location of the tungsten rods indicated. Because the incident proton beam dominates the gas production in the samples, a simpler Monte Carlo model would have produced reasonably accurate answers using less computer time. However, the model used insures that secondary particle contributions to the helium and hydrogen production are accounted for correctly. The detailed model also insures a direct comparison with the experiment because what was actually measured was not the helium or hydrogen production, but rather the helium or hydrogen atoms that slowed down and stopped in the samples and did not diffuse out of the samples. The LCS does not account for the diffusion of hydrogen and helium during irradiation and no attempt was made to correct the calculations for diffusion out of the samples during irradiation. While diffusion was not expected to be a problem with the helium comparison, the possibility of significant hydrogen diffusion out of the sample was identified as a possible error for the comparison.

Calculations of the helium and hydrogen production were carried out using versions 2.70 and 2.83 of the LCS. Because the measured results are related to the total number of helium and hydrogen atoms that are stopped in the sample volume and not necessarily the production rate in the sample, the tally option used was IOPT=14 with charged particle transport turned on in LAHET (this is not the default LAHET option).
The results are summarized in Table 3 with a comparison to the average measured values. Statistical errors on the LCS calculations were less than 3%. With the statistical error as a guideline, the LCS versions appear to have roughly the same accuracy with regards to predicting helium and hydrogen concentration in the samples in the center of the proton beam (i.e., where gas production is dominated by the primary 800-MeV proton beam). Other irradiation geometries (e.g., where secondary, lower-energy particles produce more of the helium) may lead to larger differences between the two versions of LCS. Although the statistical errors in the LAHET calculations are small, overall uncertainty is expected to be about 50%, therefore, agreement with measurements to within 50% would generally be considered as good.

Figure 6 - Monte Carlo Model of the APT Materials Irradiation

<table>
<thead>
<tr>
<th>LAHET Version</th>
<th>Gas Concentrations (appm)</th>
<th>Helium</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LAHET</td>
<td>Measured</td>
<td>Calculated</td>
</tr>
<tr>
<td>2.70</td>
<td>733</td>
<td>710</td>
<td>0.97</td>
</tr>
<tr>
<td>2.83</td>
<td>733</td>
<td>760</td>
<td>1.04</td>
</tr>
</tbody>
</table>

*aCalculated-to-measured ratio.
*bAverage of measured values for W-2 and W-3 (~2100 appm and ~3100 appm).
Discussion and Conclusions

Helium release from two irradiated tungsten samples during stepped-anneal tests was small compared to the total residual helium inventory measured in the same samples. At 1200°C, which is the postulated off-normal temperature for the APT project, the total helium release for one sample was only ~0.1%. At 1600°C, the helium release in a second sample was only slightly higher at ~0.2%. Helium release was first observed at about 800°C. One sample showed some evidence for an increasing helium release with temperature between ~800°C and ~1400°C. At the highest temperatures reached, where multiple helium analyses were conducted, both samples showed evidence of a leveling off in the helium release, suggesting helium release mechanism other than gas diffusion. Helium-3 release for both samples was at or below the detection limit of the analysis system (~10^{12} atoms) for the particular setup used in these tests. Given the low quantities of helium release at 1200°C, it is unlikely that this release will result in any pressure buildup at the target/cladding interface.

Total helium concentrations measured in the two irradiated tungsten samples had an average value of 733 ± 28 (1σ) appm, with sample W-2 being slightly higher. Review of the radiometric data from the five irradiated samples would suggest that samples W-2 through W-5 would be expected to have about the same gas production, with sample W-1 being somewhat higher. Comparison with LAHET calculations gives C/M values of 0.97 and 1.04 depending on the version of LAHET used. This is excellent agreement, however, in view of the estimated 50% uncertainty in the LAHET values, this close agreement is likely fortuitous. Absolute uncertainty (1σ) in the helium contents is estimated to be approximately 1% to 2%.

Hydrogen measurements conducted on two unirradiated samples of as-received tungsten material showed a low hydrogen impurity content of less than about 100 appm. Analyses of two irradiated samples, one at 1200°C, and the other sequentially from 750°C to 1200°C gave total hydrogen contents ranging from approximately 2100 up to possibly 3800 appm. Hydrogen levels were higher in W-1, in agreement with estimates obtained from radiometric data. The stepped temperature measurements showed hydrogen release from the tungsten at the three lower temperatures of 750°C, 900°C, and 1050°C, with the highest observed release rate (~140 appm/min) occurring at the 1050°C step. All the hydrogen had been removed from the sample by the 1200°C step.

Both analyses indicated complete hydrogen release from the tungsten at temperatures of 1200°C (or lower), within a few minutes, and suggest diffusion controlled release. Whether or not this released hydrogen will result in a pressure buildup at the target/cladding interface depends largely on whether or not any gaps exist between the tungsten and the cladding. If no gap exists, then the hydrogen will likely diffuse through the Alloy 718 at a rate equal to its release from the tungsten. If a gap exists, however, the hydrogen will likely recombine to molecular H₂, and release through the cladding may be slow.

Comparison of the hydrogen values with LAHET calculations gives C/M values of 1.90 and 1.92, again depending on the version of LAHET used. Some of the discrepancy between the calculated and measured values is undoubtedly the result of the combined uncertainties in both the measurements and the calculations (about 50% each). In addition, there was expected to be some diffusion of hydrogen out of the tungsten during the irradiation which would result in measured values being lower than calculated.
Within the respective uncertainties of the gas measurements and calculations, several observations can be made:

- Significant levels of helium and hydrogen were measured in the irradiated tungsten target material. Hydrogen levels in unirradiated material were less than ~100 appm.
- Helium release at the postulated off-normal temperature of 1200°C is small at about 0.1 to 0.2% of the total generated helium. Helium release first occurs at ~800°C, and the release rate does not change significantly with temperature. Multiple helium measurements conducted at 1200°C and 1600°C showed a leveling off of the helium release with time, suggesting release mechanisms other than gas diffusion.
- Given the small levels of helium released, helium gas buildup should not contribute significantly to any pressure buildup at the target/cladding interface.
- Hydrogen release was seen to occur at the lowest temperature of 750°C employed in the present analyses, with the highest observed release rate occurring at the 1050°C step, suggesting diffusion controlled release.
- Essentially complete release of generated hydrogen occurred at a temperature of 1200°C within a few minutes. Whether or not this released hydrogen will contribute to a pressure buildup at the target/cladding interface will depend on whether there is a gap at the interface.
- LAHET calculations of gas generation in the target tungsten generally agreed well with measurements within estimated uncertainties.

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REFERENCES


