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Hydrogen release from 800 MeV proton-irradiated tungsten

B.M. Oliver [a,*], T.J. Venhaus [b], R.A. Causey [b], F.A. Garner [a], S.A. Maloy [c]

[a] *Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, USA*
[b] *Sandia National Laboratory, Livermore, CA 94550, USA*
[c] *Los Alamos National Laboratory, Los Alamos, NM 87545, USA*

Abstract

Tungsten irradiated in spallation neutron sources, such as those proposed for the accelerator production of tritium (APT) project, will contain large quantities of generated helium and hydrogen gas. Tungsten used in proposed fusion reactors will also be exposed to neutrons, and the generated protium will be accompanied by deuterium and tritium diffusing in from the plasma-facing surface. The release kinetics of these gases during various off-normal scenarios involving loss of coolant and after heat-induced rises in temperature are of particular interest for both applications. To determine the release kinetics of hydrogen from tungsten, tungsten rods irradiated with 800 MeV protons in the Los Alamos Neutron Science Center (LANSCE) to high exposures as part of the APT project have been examined. Hydrogen evolution from the tungsten has been measured using a dedicated mass-spectrometer system by subjecting the specimens to an essentially linear temperature ramp from ~300 to ~1500 K. Release profiles are compared with predictions obtained using the Tritium Migration Analysis Program (TMAP4). The measurements show that for high proton doses, the majority of the hydrogen is released gradually, starting at about 900 K and reaching a maximum at about 1400 K, where it drops fairly rapidly. Comparisons with TMAP show quite reasonable agreement using a trap energy of 1.4 eV and a trap density of ~7%. There is a small additional release fraction occurring at ~550 K, which is believed to be associated with low-energy trapping at or near the surface, and, therefore, was not included in the bulk TMAP model.
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1. Introduction

The accelerator production of tritium (APT) project [1] was proposed as one of several techniques available to the US for production of tritium. In the APT concept, high-energy protons impinge on a tungsten target producing high-energy spallation neutrons. These neutrons are multiplied and then thermalized. Tritium production occurs through capture of the thermalized neutrons by ^{3}He gas.

To address various issues related to radiation damage under high-energy proton and neutron fluxes, a materials irradiation program using the 800 MeV proton accelerator at the Los Alamos Neutron Science Center (LANSCE) was developed [2]. To simulate the tungsten neutron source in the proposed APT target, a series of tungsten rods were included in the materials irradiation assembly. After extended exposure in the LANSCE beamline, the tungsten samples were removed, sectioned, and then analyzed for hydrogen and helium content as reported earlier [3].

In this earlier work, hydrogen release was also measured in one of the tungsten samples as a function of temperature from ~300 to ~1500 K. The release measurements were conducted using a non-linear temperature ramp and showed separate release peaks at temperature of approximately 770, 1070, 1270, and 1370 K, suggesting multiple trapping sites. These release data were subsequently compared [4] with theoretical predictions obtained using the Tritium Migration Analysis Program (TMAP4). Using literature values for the

* Corresponding author. Tel.: +1-509 376 9228; fax: +1-509 372 2156.
E-mail address: brian.oliver@pnl.gov (B.M. Oliver).

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material parameters, and only a single trap at energy 1.4 eV, the model predicted the general release behavior quite well. However, a second simulation performed using a 'true' linear temperature ramp did not show any of the peaks, but rather a slow release from the material that peaked at ~1500 K and then decayed with time. This suggested that the 'peaks' observed were an artifact of the non-linear nature of the temperature ramp used.

To resolve the problems associated with the earlier non-linear temperature profile, a series of new measurements of hydrogen release from additional samples of tungsten irradiated in the APT materials program have been undertaken and are reported here. These new measurements were conducted at linear temperature ramp rates of 50 and 100 K/min, and are compared with new model predictions using the TMAP4 code.

2. Tungsten samples

The tungsten samples were prepared at Los Alamos National Laboratory (LANL). Each sample was in the form of a thin disk, approximately 0.25 mm thick, cut from a single 3.18 mm diameter tungsten target rod irradiated with 800 MeV protons in LANSCE between September and November 1996. The tungsten rod was formed by powder metallurgy (pressed, sintered and then drawn) and had an elemental composition of 99.96% tungsten with the major impurities being Mo at 100 μg/g and C and O at 30 μg/g each. The initial grain size was ~15 μm. Proton fluence for the in-beam sample (1Wh) was $\sim 1.1 \times 10^{21}$ p/cm^2 and for the out-of-beam sample (1Wc) $\sim 4 \times 10^{19}$ p/cm^2. Calculated displacement rates were 7.9 and 0.31 dpa, respectively. The radial temperature of the rods is estimated to have ranged from ~440 (surface) to ~450 K (center) at beam center, to ~310 K out of the beam.

Specimens for hydrogen analysis were cut from each disk using small diagonal cutters. Each specimen was individually cleaned in acetone and air-dried, and the mass 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.

3. Hydrogen analysis system

Hydrogen release measurements were conducted using a gas mass-spectrometric analysis system, the details of which have been reported elsewhere [5]. The analysis procedure involved dropping the individual specimens, under vacuum, into a small cylindrical ceramic crucible. Prior to analysis, the analysis crucible was pre-heated to approximately 1300 K under high vacuum for several days. During the pre-heating and subsequent analysis, the sample chamber was maintained at approximately room temperature.

Hydrogen release was measured as a function of time using a quadrupole mass spectrometer connected to the crucible volume. Calibration of the system sensitivity was accomplished using a calibrated hydrogen leak source with a stated absolute uncertainty of ±15%. Calibration measurements were conducted before and after each sample analysis, and showed an overall reproducibility of 2–3%.

4. Hydrogen release measurements

In the present experiment, hydrogen measurements were conducted on sections taken from two of the disk samples discussed in Section 2, and on two samples of un-irradiated tungsten material from the same batch. In these measurements, the temperature of the sample was ramped from ~300 up to ~1500 K in an essentially linear profile of either 50 or 100 K/min depending on the expected total hydrogen in the sample. The results from one of the two un-irradiated samples, and both irradiated samples, are shown in Figs. 1–3. In each plot, the thick solid line is the crucible temperature profile (right axis) as a function of heating time in seconds (lower axis). The thinner solid line in each plot is the measured instantaneous hydrogen release in atoms per second (left y-axis), again as a function of heating time. Sample mass (mg), proton damage dose (dpa), and total integrated hydrogen release in atomic parts per million (appm) are also indicated in each plot.

Integrated hydrogen releases for all the samples analyzed are in good agreement with those reported earlier using a rapid heating method [3]. The two un-irradiated controls showed an average hydrogen release of $(162 \pm 35\ (1\sigma))$ appm, which is in good agreement with the previous measurements which showed 212 ± 30 appm. Integrated hydrogen measured in the low-dose tungsten sample (1Wc) was 448 appm compared to a previous average of 432 ± 66 appm. Hydrogen measured in the high-dose sample (1Wh) was 1990 appm compared to the previous 2200 ± 480 appm value.

The release curves for the tungsten controls and sample 1Wc are similar in that they show a single major release peak at about 550 K. There is also a small release peak in sample 1Wc at about 1400 K. The release curve for the high proton dose sample (1Wh) looks quite different, and is close to the TMAP4 predictions reported earlier [4] for a faster linear ramp rate of 160 K/min. Here, there is still a small peak at ~550 K, but the majority of the hydrogen starts to come out at ~900 K and peaks at ~1400 K.

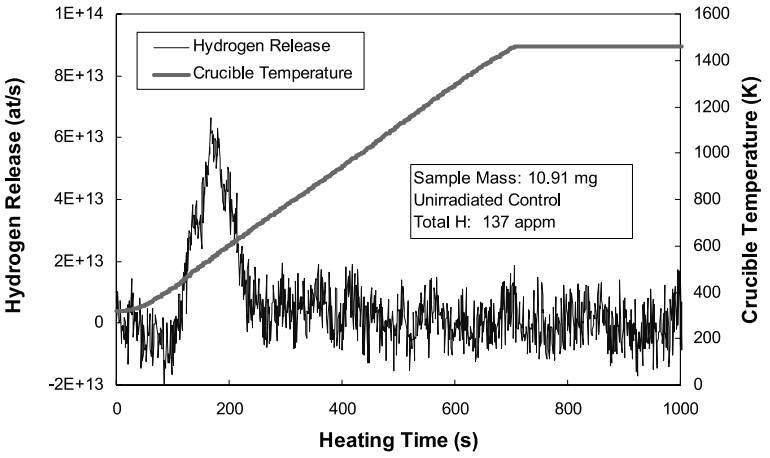

Fig. 1. Hydrogen release in un-irradiated tungsten material.

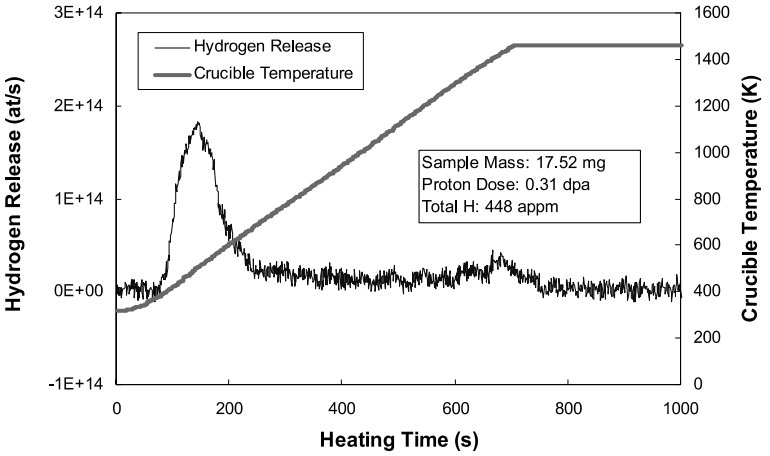

Fig. 2. Hydrogen release in low-dose proton-irradiated tungsten (1Wc).

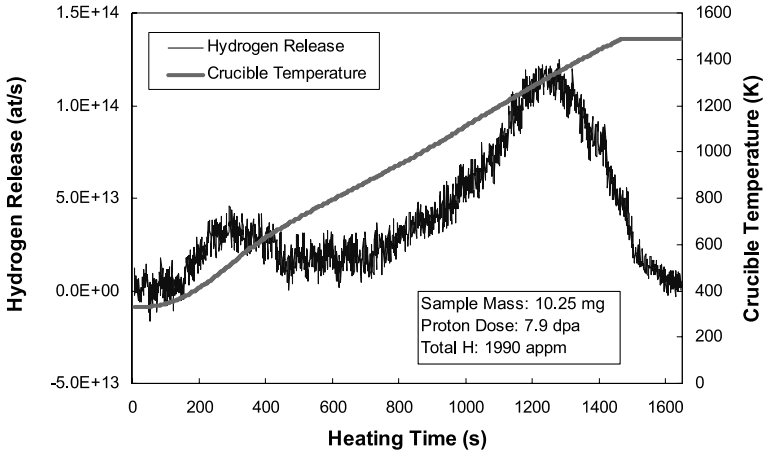

Fig. 3. Hydrogen release in high-dose proton-irradiated tungsten (1Wh).

5. Modeling

The Release of hydrogen from the tungsten samples was modeled using the TMAP4 developed at INEEL [6]. TMAP4 is a finite-difference computational code capable of simultaneous calculation of hydrogen migration and thermal transport through materials. The 1-D model is developed by first defining a material of a certain thickness, then defining all transport parameters appropriate to hydrogen migration, trapping, and release from the material. These parameters are diffusivity, recombination rate coefficient, and trapping. A review of these parameters and others affecting hydrogen retention and migration in tungsten has been given by Causey and Venhaus [7]. Based on this review, the diffusivity of hydrogen in tungsten given by Frauenfelder [8], i.e., $D = 4.1 \times 10^{-7} \exp(-0.39\ \mathrm{eV/kT})\ \mathrm{m^2/s}$, was used in the simulations. It is also assumed that recombination will not slow the release process during the thermal desorption experiments.

The last parameter affecting the release rate of hydrogen is trapping. There are several types of defects that might lead to trapping of hydrogen in tungsten; dislocation at cell boundaries [9], vacancies [10], and voids [10–12]. Anderl et al. [9] showed a direct correlation between the removal of dislocations on cell boundaries and a decrease in the number of hydrogen traps. The trap energy was estimated to be 1.3–1.5 eV. Eleveld and Van Veen [10] showed the energy of the trap associated with the vacancies was 1.4 eV. Lastly, Van Veen et al. [12] and Eleveld and Van Veen [10,11] showed hydrogen to be trapped at voids with an effective energy of 1.4 eV. It should be noted that it is a coincidence that dislocations, vacancies, and voids all trap hydrogen with a trap energy of ~1.4 eV.

Trap energy values from 1.2 to 1.6 eV were used in the earlier simulations for the hydrogen release from tungsten [4]. It was found that a value of 1.4 eV resulted in the best agreement with the experimental data, and this value was again assumed here. Therefore, the trap concentration and the level of trap filling were the only fit parameters used in the present TMAP model. The trap density was adjusted to give a 'best fit' to the measured hydrogen release profiles, and the percentage of traps filled was adjusted to yield the total measured hydrogen content. Only that portion of the hydrogen release associated with the high-temperature trap was modeled. The sample geometry was assumed to be an essentially infinite slab with a thickness of ~0.25 mm.

6. Comparison with TMAP predictions

The low-temperature release peaks at about 550 K, noted in both the un-irradiated material and in the proton-irradiated material, are assumed to be associated with a non-bulk surface or near-surface trapping mechanism. From the work of Anderl et al. [9], it is known that 1.3–1.6 eV traps exist at moderate levels (~70 appm) throughout all un-annealed tungsten samples. The samples used in this experiment were not annealed. If bulk trapping of hydrogen at a low-energy trap (0.5–0.7 eV) existed for a tungsten sample, thermal desorption of hydrogen from that sample would exhibit a release of some of the hydrogen at a lower temperature, but the majority of the hydrogen would be released at higher temperatures as a result of re-trapping of the hydrogen in the higher energy traps on its way to the surface.

The un-irradiated sample in the present work showed most of the hydrogen release in a single low-temperature peak, suggesting the hydrogen must have originated at the surface, perhaps associated with a thin oxide layer. The two control samples also showed a release peak at lower temperature, and this hydrogen is also believed to be associated with a small amount of surface trapping. Such surface trapping cannot be modeled by TMAP. Thus, for the purposes of comparison with the TMAP code, only that portion of the hydrogen release associated with the high-temperature trap was modeled. Deconvolution of the release profile for the two proton-irradiated samples yields total integrated hydrogen releases from the high-temperature traps of ~80 appm for sample 1Wc and ~1690 appm for sample 1Wh.

TMAP model predictions for the hydrogen release from the two irradiated samples are shown in Figs. 4 and 5 (solid triangles with lines) for a trap energy of 1.4 eV and density of 7.5% relative to the number of lattice sites. Also included on each plot are the actual measured data (thin solid line) and the temperature profile (thick solid line) used for the TMAP predictions. Predicted hydrogen release is given as atoms/s $\mathrm{m^2}$ for one side of the slab sample. The trap density of 7.5% was empirically arrived at to yield a best fit to the high-temperature release profiles for both samples. It should be noted, however, that reasonable fits to the data could also be obtained with trap densities as low as ~4%. This level of trap density is significantly higher than observed by Anderl et al. [9] for un-irradiated, un-annealed material, suggesting that most of the traps are created by the energetic proton beam. While trapping at this level seems difficult to imagine, it must be remembered that the 1.4 eV trap can be dislocations, vacancies, or voids. This is a material that has undergone proton damage equal to 7.9 dpa at a relatively low irradiation temperature. In the modeling for each sample, the trap filling level was adjusted to give a total hydrogen concentration in agreement with that measured, i.e., 80 and 1690 appm, respectively. The measured hydrogen releases were normalized to the TMAP data using the calculated surface area of each sample assuming a slab geometry with no correction for edge effects.

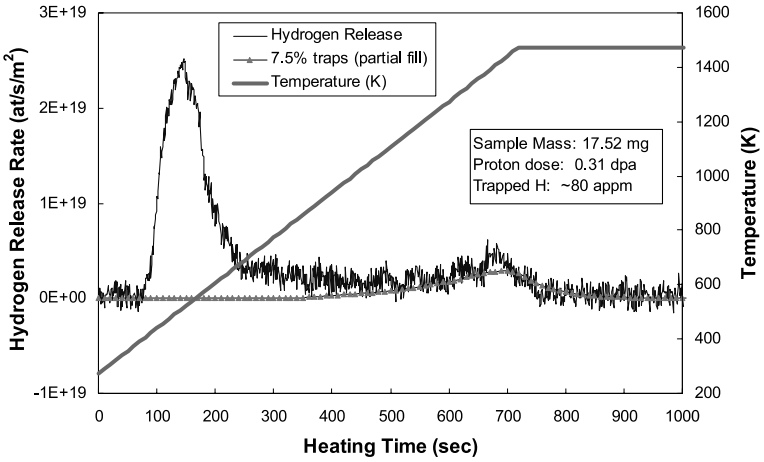

Fig. 4. Comparison of measured and TMAP-predicted hydrogen release for sample 1Wc.

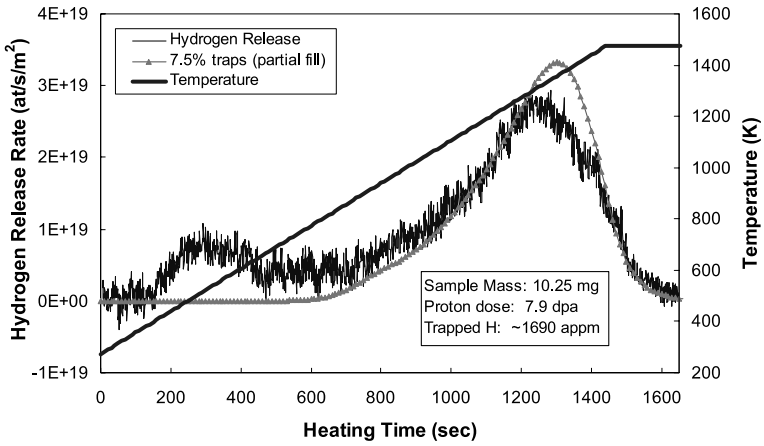

Fig. 5. Comparison of measured and TMAP-predicted hydrogen release for sample 1Wh.

Examination of Fig. 5 for the high proton dose sample 1Wh shows quite reasonable agreement with the TMAP predictions for the high-temperature part of the release. Although much smaller in level, the TMAP predictions for the same trap density, but with lower filling levels, also show reasonable agreement for the high-temperature release in the low proton dose sample 1Wc. The fact that the same trap density yields reasonable agreement for both samples, even though the proton damage doses are significantly different, suggests a saturation effect in the trap formation by the energetic protons.

Several attempts were also made to use TMAP to model both temperature release peaks observed in both irradiated samples. These runs were made by assuming lower trap densities, but under conditions where the traps are all filled. Additional 'free' hydrogen was then added to yield total hydrogen contents in agreement with those measured. Without traps, or with an excess of free hydrogen, TMAP does indeed predict a low-temperature release component. However, under these conditions of low trap density, the high-temperature release is shifted significantly lower in temperature. As a result, no combination of trap density and free hydrogen level was found to give agreement with the observed data, further suggesting that the low-temperature releases are due to a non-bulk surface component.

7. Conclusion

Hydrogen release from tungsten material irradiated with 800 MeV protons in the LANSCE facility has been

investigated. In earlier measurements [4], several peaks were observed in the thermal desorption spectrum from a single tungsten sample, suggesting multiple trapping sites. Modeling of the release behavior using the TMAP code and a single trap energy of 1.4 eV, however, indicated that the peaks were a result of non-linearities in the temperature ramp used for the measurements.

New measurements are reported here of hydrogen release from two additional samples of the same LANSCE-irradiated tungsten material and two un-irradiated samples from the same lot. The measurements show a single release peak at ~550 K for the un-irradiated samples, and two release peaks, one at ~550 K and the other at ~1400 K for the irradiated samples. The low-temperature release is reasonably consistent in total hydrogen between the samples, and is assumed to be from non-bulk surface trapped hydrogen. The high-temperature release for the two samples irradiated at quite different proton doses both show quite reasonable agreement with TMAP4 predictions using a trap energy of 1.4 eV and a trap density in the range of 4–7%. The high trap levels suggest formation by the proton beam, with a possible saturation effect. Additional modeling runs attempting to simulate both release peaks were not successful, supporting the conclusion that the low-temperature hydrogen component is related to a surface or near-surface effect. Total integrated hydrogen releases from the samples are in good agreement with earlier measurements conducted using a rapid heating process [3].

In terms of the APT project, the release observed here was for a small sub-sample of the original tungsten rod. The fractional release rate for the entire rod will be significantly slower. For fusion applications, the ability of the TMAP code to closely fit the data suggests that it should be possible to accurately predict the tritium inventories for large fusion devices.

Acknowledgements

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