Tritium retention in tungsten exposed to intense fluxes of 100 eV tritons

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Abstract

Tungsten is a candidate material for the International Thermonuclear Experimental Reactor (ITER) as well as other future magnetic fusion energy devices. Tungsten is well suited for certain fusion applications in that it has a high threshold for sputtering as well as a very high melting point. As with all materials to be used on the inside of a tokamak or similar device, there is a need to know the behavior of hydrogen isotopes embedded in the material. With this need in mind, the Tritium Plasma Experiment (TPE) has been used to examine the retention of tritium in tungsten exposed to very high fluxes of 100 eV tritons. Both tungsten and tungsten containing 1% lanthanum oxide were used in these experiments. Measurements were performed over the temperature range of 423–973 K. After exposure to the tritium plasma, the samples were transferred to an outgassing system containing an ionization chamber for detection of the released tritium. The samples were outgassed using linear ramps from room temperature up to 1473 K. Unlike most other materials exposed to energetic tritium, the tritium retention in tungsten reaches a maximum at intermediate temperatures with low retention at both high and low temperatures. For the very high triton fluences used ($>10^{25}$ T/m^2), the fractional retention of the tritium was below 0.02% of the incident particles. This report presents not only the results of the tritium retention, but also includes the modeling of the results and the implication for ITER and other future fusion devices where tungsten is used. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Tungsten is a candidate plasma-facing material for use in the International Thermonuclear Experimental Reactor (ITER) as well as other advanced fusion devices. This material has a high threshold for sputtering as well as a very high melting temperature. As a plasma-facing material, tungsten may be exposed to extremely high fluxes of energetic hydrogen isotope ions and neutrals. From a recycling point of view as well as a tritium inventory point of view, an understanding of the reten-

tion and migration of hydrogen isotopes embedded in tungsten is vitally important. This report helps provide an understanding of these processes by describing the results of a study of the retention of plasma delivered tritium in both tungsten and tungsten doped with 1% lanthanum oxide. The doped material has been selected as the primary candidate for use in ITER.

Tungsten and lanthanum oxide doped tungsten disks were placed in the Tritium Plasma Experiment (TPE) where they were exposed to plasmas consisting of deuterium and tritium. A 100 eV particle flux of 8.7×10^{21} (D + T)/m^2 s for all experiments. Exposure times were varied between 1 and 4 h with temperatures between 423 and 973 K. Total hydrogen isotope retention was determined by measuring the amount of tritium released during thermal outgassing of the samples and then correcting for the isotope concentrations in the plasma. Several of the samples were also profiled for deuterium

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concentration as a function of depth using nuclear reaction profiling.

2. Experimental procedures

The samples used in these experiments were provided by Plansee Aktiengesellschaft. Both the 'pure' and lanthanum oxide doped samples were powder metallurgy products. The pure tungsten was 99.99% tungsten while the doped material contained 1% lanthanum oxide. The lanthanum oxide doping was developed by Plansee Aktiengesellschaft to increase the machinability of the material. After receipt, all samples were annealed at 1273 K for 1 h in an inert atmosphere. The pure tungsten samples were polished after the annealing.

All experiments were performed in the TPE. This arc reflex plasma source has been described elsewhere [1]. During plasma exposure, the samples were negatively biased to increase the energy of the deuterium and tritium ions striking the sample surfaces to 100 eV. In TPE, the intensity of the plasma is controlled by varying the voltage and temperature of the cathode. For all experiments reported here, the total flux was held at 8.7×10^{21} (D + T)/m^2 s.

The heating of the 50.8 mm diameter, 2 mm thick, samples was provided by the plasma itself. An outer tungsten ring was used to press the sample disk and two accompanying disks against the water-cooled copper plate. The disk immediately behind the sample was composed of copper to help maintain a level temperature distribution. The third disk (the one in contact with the water-cooled holder) was varied in composition (copper, aluminum, or stainless steel) and geometry (holes or grooves were used to lower the effective thermal diffusion area) to allow different temperatures to be obtained from the same heat flux. All of the sample disks were 2 mm thick. The sample temperature was measured with a thermocouple passing through holes in the two backing disks and pressing directly against the rear of the sample.

Gas consisting of 3% tritium and 97% deuterium was fed into the system at a rate of 30 cc(stp)/min. The isotope abundance of the feed gas was used to convert the measured amount of tritium into total hydrogen isotope retention. A 2200 l/s turbomolecular pump located directly under the sample chamber maintained the total pressure in the system at 0.04 Pa. The primary impurity in the system was water vapor at a partial pressure of approximately 1.5×10^{-5} Pa.

After the plasma exposure, the samples were transferred in air to the outgassing system where the temperature was ramped from room temperature up to 1473 K at a rate of 20 K/min. Gas consisting of 99% helium and 1% hydrogen was swept over the sample and through an ionization chamber where the amount of tritium was continuously recorded.

3. Experimental results and discussion

The experimental results for the tritium retention in the plasma exposed tungsten samples are shown in Fig. 1 (lines are intended only to guide the eye). All samples were exposed to a 100 eV tritium/deuterium flux of 8.7×10^{21} (D + T)/m^2 s for 1 h. The retention was determined by thermal desorption during a linear ramp of the furnace from room temperature up to 1473 K. The released tritium was detected by sweeping it out of the furnace and through an ionization chamber. It can be seen in the figure that the tritium retention is low at both lower and higher temperatures with a local maximum in retention at about 600 K for the pure tungsten and a little over 700 K for the lanthanum oxide doped material. A similar localized peak in deuterium retention was reported by Haasz et al. [2] in their studies on 300, 500, and 1000 eV deuteron retention in doped and undoped tungsten. The localized maximum in the retention suggests that the migration of tritium in tungsten is being affected by some type of trapping. This conclusion is backed by the structure seen in the thermal desorption spectra shown in Figs. 2 and 3. These data show one peak in the desorption rate at slightly above 1000 K and a second peak or shoulder at slightly below 1400 K. Two additional peaks at approximately 600 and 800 K were seen in the outgassing of the undoped tungsten. These samples were polished after the 1273 K annealing. It is believed that the cold working resulted in additional trapping in the near-surface region. The third piece of evidence that trapping was occurring for the tritium in the tungsten was the nuclear reaction profiling that was measured for four of the samples exposed only to a deuterium-only plasma. Those results are shown as Figs. 4 and 5. When these results are compared to the retention results, it can be calculated that between 25% and 50% of all of the hy-
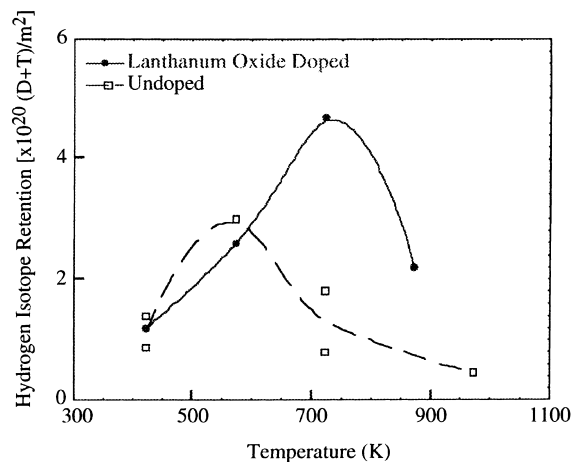

Fig. 1. Hydrogen isotope retention in doped and undoped tungsten.
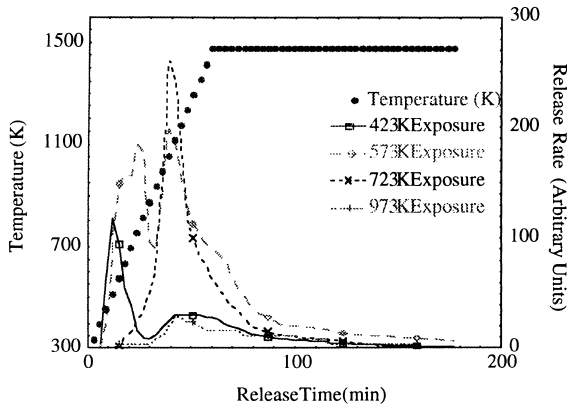
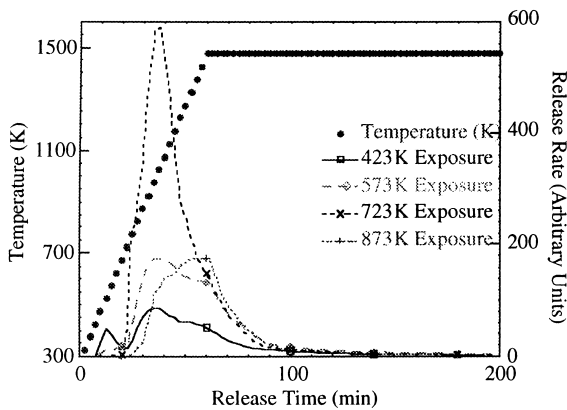Fig. 2. Hydrogen isotope release rate during thermal desorption of undoped tungsten.

Fig. 3. Hydrogen isotope release rate during thermal desorption of lanthanum oxide doped tungsten.
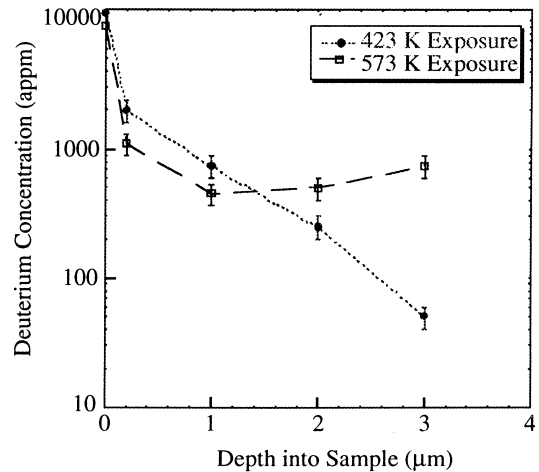

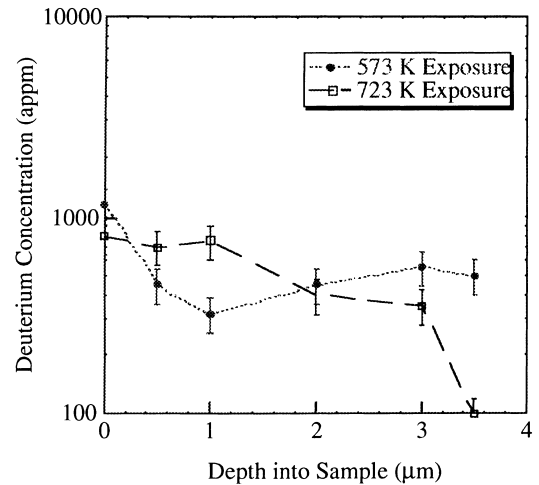Fig. 4. Nuclear reaction profiling results for deuterium plasma exposed undoped tungsten.

Fig. 5. Nuclear reaction profiling results for deuterium plasma exposed lanthanum oxide doped tungsten.

drogen isotopes retained in the tungsten samples was located in the first 3–5 microns of the plasma exposed side.

Most of the samples were outgassed several days after exposure to the tritium plasma. Two samples, both pure tungsten, were transferred immediately from the plasma device to the outgassing system. In less than 1 h from the time the samples were exposed, they were placed in the outgassing system where the release was monitored overnight. The release rate was fit to a power function to predict the release rate during the short time between plasma exposure and placement in the outgassing system. For the sample exposed at 423 K, approximately 20% of the total retention was released at room temperature. For the sample exposed at 573 K, the room temperature release equaled 8% of the total. Most of this room temperature release occurred in the first few hours and represents the non-trapped tritium.

An attempt was first made to model only the tritium retention results without the additional constraints implied by the complicated structure in the thermal desorption spectra or the obvious trapping in the near-

surface region as seen in the deuterium profiling. While there is some difference in the results for the two different types of tungsten examined in this report, only the results from the lanthanum oxide doped material were modeled. This is due to the importance of this material to the ITER program. The literature on hydrogen isotope migration in tungsten [2–11] was scanned to determine the consensus values to use for the various migration parameters. For the diffusivity of hydrogen in tungsten, the expression provided by Frauenfelder [3] was used in the majority of recent reports. Frauenfelder reported an activation energy for hydrogen diffusion in tungsten to be 0.39 eV with a pre-exponential coefficient of 4.1×10^{-7} m^2 s. There was much less of a consensus in the literature for the trapping density and energy. In the following discussion, the term trap energy is assumed

to be the binding energy of the trap plus the diffusion energy. Garcia-Rosales et al. [4] reported two trap sites, one at 0.85 eV with a density of 0.01 trap/W and a second at 1.4 eV with a density of 0.07 trap/W. From thermal desorption data, Franzen et al. [5] gave one trap at 0.5 eV with a trap/W value of 0.01 and a second at 1.2 eV with 0.16 trap/W existing only in the implantation zone. Anderl et al. [6] reported their deuterium transport in polycrystalline tungsten to be dominated by a 1.34–1.56 eV trap that decreased in concentration due to annealing. The unannealed density was quoted as 6.9×10^{-5} trap/W, decreasing to 2.6×10^{-5} for a 1273 K anneal, and then down to 1.3×10^{-5} for a 1673 K anneal. To simplify the modeling at this point, a single trap energy of 1.4 eV was assumed with a density of 2.6×10^{-5} trap/W throughout the entire sample. This is consistent with the measurements of Anderl et al. [6] with a 1273 K anneal. While recombination limited kinetics was invoked in most of the above references, a simple C = 0 at the surface was assumed for the present modeling. A comparison of the measured values for the lanthanum oxide doped samples and the values determined by the DIFFUSE [12] computer code assuming the above parameters is shown in Fig. 6. It can be seen in the figure that this model significantly overestimates the low temperature retention of tritium.

One possible explanation of the difference between the measured and predicted tritium retention is that the diffusivity in the implant zone is incorrect. Repeated attempts at changing other parameters such as overall diffusivity, trap energy, trap density, and the surface boundary condition did not improve the fit of the model to the data. It is not difficult to imagine that the implantation of 8.7×10^{21} (D + T)/m² s into a thickness of

only about 10 nm would result in the continuous 'agitation' of the atoms in this region. Assuming the diffusivity in the implant zone to be a constant 4×10^{-9} m²/s (no dependence on temperature), gave the correct shape for the retention, but underestimated the retention at all temperatures. This was then corrected by increasing the trapping in the sample to match that seen in the nuclear reaction modeling. A trapping density of 400 appm was assumed for the entire sample. The comparison of the modified model prediction and the measured retention is now shown in Fig. 7. It can be seen in the figure that the above changes significantly improved the ability of the computer code to model the tritium retention as a function of temperature. The changes also improved the prediction of the tritium retention in the near surface region (the code now predicted the traps in the first several microns of the samples to be completely filled for the temperatures where the nuclear reaction profiling measurements were performed).

Problems with this improved model became obvious when an attempt was made to model the outgassing results. Fig. 8 shows a comparison of the model predictions and experimental data for a doped sample exposed to the plasma for 1 h at 573 K. The location of the single peak in the computer prediction agrees fairly well with the first peak at about 1100 K in the desorption data. The peak or shoulder at 1400 K seen in the experimental data for both doped and undoped tungsten is completely missing in the model prediction. While part of the difference in the two curves can be explained by the broadening of the desorption data caused by the several minute long residence time for the released gas in both the furnace and the ionization chamber, there is obviously a second type of trap responsible for the delayed release.
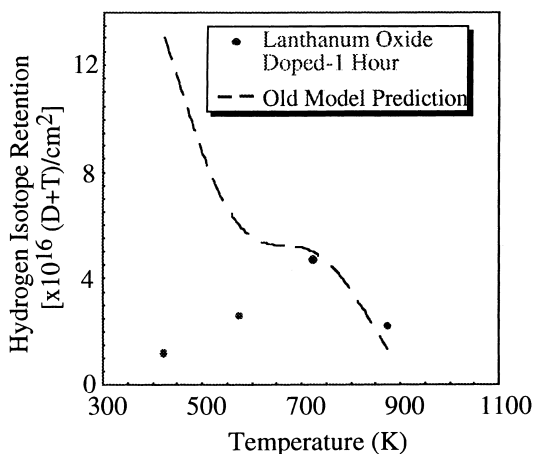

Fig. 6. Comparison of the measured hydrogen isotope retention in lanthanum oxide doped tungsten versus that predicted by a model utilizing accepted values for migration parameters.
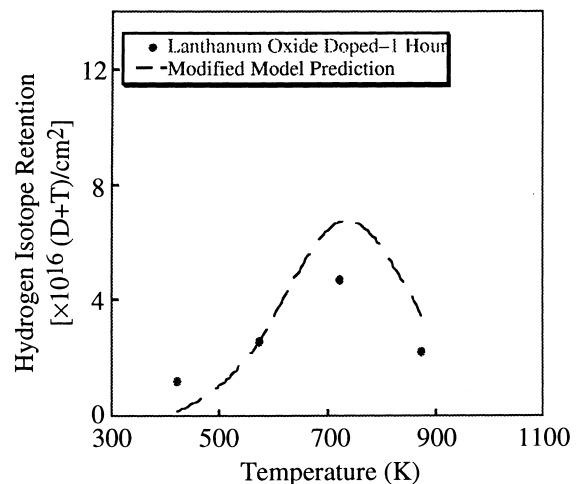

Fig. 7. Comparison of the measured hydrogen isotope retention in lanthanum oxide doped tungsten versus that predicted by a modified model using enhanced diffusion in the implant zone.
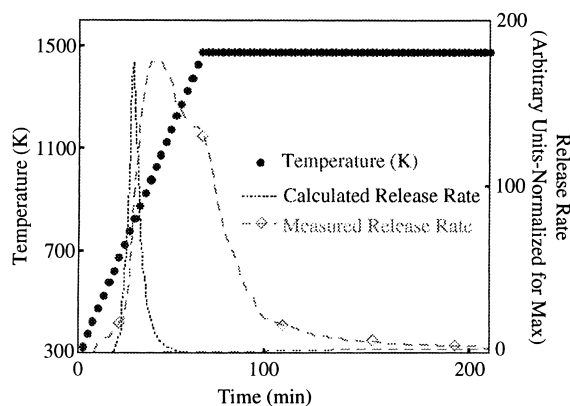
Fig. 8. Comparison of the measured and calculated hydrogen isotope release from doped tungsten exposed to the plasma at 573 K.

An attempt at correcting the model by the inclusion of a second trap energy did improve the fit of the outgassing data to the model, but this change resulted in the prediction of very high retention values at high temperatures. There was no combination of two simple traps that would meet simultaneously the requirement of decreasing tritium retention with increasing temperature above 800 K and yield a peak or shoulder in the outgassing rate that would appear at 1400 K.

It is postulated that the second trap involves the formation of hydrogen isotope molecules at voids or defects in the samples. The formation of molecules would explain the decreasing concentration of tritium in the samples at higher temperatures at the same time that a higher energy trap is allowed. For the higher energy trap (the formation of a molecule) to occur, it is necessary that a mobile tritium encounter another tritium already existing at the defect. Because the number of trapped atoms rapidly decreases as the temperature is increased above about 700 K, there are very few precursors for the formation of the higher energy molecular traps. Still, once formed, the molecules are expected to remain stable. It is believed that for the temperatures and fluences where these measurements were performed, the molecular formation does not lead to large bubbles or voids. This conclusion is based on both SEM and TEM examination of the samples after exposure that showed no visible bubbles or blisters. Modeling of the formation of molecules in plasma exposed samples will be pursued in the future.

4. Summary

Tritium retention measurements have been performed on powder metallurgy samples of relatively pure tungsten and tungsten doped with 1% lanthanum oxide. The samples were exposed to intense 100 eV tritium and deuterium particles at temperatures from 423 to 973 K. Measured retention of tritium and deuterium reached a maximum at about 600 K in the undoped material and about 700 K in the doped material. Overall, the retention values were much less than those predicted using reported values for the diffusivity, recombination rate coefficients, and trapping. Nuclear reaction profiling of samples exposed to a deuterium only plasma showed the trapped concentration of deuterium to saturate at about 400–500 appm and extend several microns into the samples. Thermal desorption spectroscopy of plasma exposed samples showed the release to be governed by two traps, one at about 1.4 eV and another at about 2.5–2.8 eV. The second trap is postulated to be due to the formation of molecules at defects in the samples.

References

[1] R.A. Causey, D. Buchenauer, W. Harbin, D. Taylor, R. Anderl, Fusion Technol. 28 (3) (1995) 1144.
[2] A.A. Haasz, J.W. Davis, M. Poon, R.G. Macaulay-Newcombe, J. Nucl. Mater. 258–263 (1998) 889.
[3] R. Frauenfelder, J. Vac. Sci. Technol. 6 (1969) 388.
[4] C. Garcia-Rosales, P. Franzen, H. Plank, J. Roth, E. Gauthier, J. Nucl. Mater. 233–237 (1996) 808.
[5] P. Franzen, C. Garcia-Rosales, H. Plank, V.Kh. Alimov, J. Nucl. Mater. 241–243 (1997) 1082.
[6] R.A. Anderl, D.F. Holland, G.R. Longhurst, R.J. Pawelko, C.L. Trybus, C.H. Sellers, Fusion Technol. 21 (1992) 745.
[7] A.A. Haasz, J.W. Davis, J. Nucl. Mater. 241–243 (1997) 1076.
[8] R.A. Anderl, R.J. Pawelko, M.R. Hankins, G.R. Longhurst, R.A. Neiser, J. Nucl. Mater. 212–215 (1994) 1416.
[9] V.Kh. Alimov, B.M.U. Scherzer, J.Nucl. Mater. 240 (1996) 75.
[10] A.A. Pisarev, A.V. Varava, S.K. Zhdanov, J. Nucl. Mater. 220–222 (1995) 926.
[11] H. Eleveld, A. van Veen, J. Nucl. Mater. 191–194 (1992) 433.
[12] M.I. Baskes, SAND83-8231, 1983.