Journal of Nuclear Materials 390–391 (2009) 717–720

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Defects in tungsten responsible for molecular hydrogen isotope retention after exposure to low energy plasmas

R.A. Causey [a], R. Doerner [b], H. Fraser [c], R.D. Kolasinski [a,*], J. Smugeresky [a], K. Umstadter [b], R. Williams [c]

[a] Sandia National Laboratories, MS9402, P.O. Box 969, Livermore, CA 94550, USA
[b] University of California San Diego, San Diego, CA, USA
[c] Ohio State University, Columbus, OH, USA

ARTICLE INFO

PACS:
61.16.Bg
66.30.−h
67.55.Hc

ABSTRACT

Recent work on hydrogen isotope retention in tungsten has shown a substantial fraction of the retained hydrogen to be in the form of molecules. It can be expected that hydrogen permeating through a material such as tungsten, that has a very low solubility for hydrogen, would come out of solution and combine into molecules at voids located throughout the bulk. The purpose of this report is to determine the type of voids responsible for the molecular retention. High purity tungsten provided by Plansee Aktiengesellschaft was first polished, annealed at 1273 K in vacuum for one hour, and then exposed to high fluxes and high fluences of deuterium in the PISCES facility. High resolution Transmission Electron Microscopy was then used to examine the samples for voids. The results of these experiments were used to interpret the expected behavior of tungsten to be used as the divertor of the ITER fusion device.

1. Introduction

The interaction of high fluxes of low energy hydrogen isotopes with tungsten has been studied intensely over the last several years in preparation for ITER. Most of these studies have been covered in reviews by Alimov and Roth [1], Zakharov et al. [2], Ogorodnikova et al. [3], and Causey [4]. Attempts at modeling the retention and thermal desorption of hydrogen isotopes in tungsten [5–8] based on atomic trapping alone have shown inconsistencies in such a model. The relatively recent results by Alimov and Roth [1] and Alimov et al. [9] that hydrogen is also retained in tungsten in the molecular form after low energy plasma exposure may explain these inconsistencies. Hydrogen retention and release in bubbles or voids in tungsten would behave differently from that of trapped atoms.

While earlier papers by van Veen and Eleveld [10–12] showed rather conclusively that hydrogen could be contained in voids created by high energy implantation, little consideration was given to the possibility that the same could exist for intense fluxes of low energy hydrogen. While others such as Causey et al. [7] speculated on the existence of molecular hydrogen in tungsten exposed to high fluences of low energy hydrogen isotopes because of difficulty in modeling the trapping as single site atoms, and many [13–19] reported on blistering, no proof of molecular trapping deep into the tungsten from low energy hydrogen existed prior to the work of Alimov and Roth [1] in 2007. Alimov et al. [20,21] laid the ground work for detecting the molecular hydrogen in tungsten in a set of experiments on higher energy implantation. They used a secondary ion mass spectrometry (SIMS) technique to separate atomic deuterium from molecular deuterium as the beam etched itself through the sample. The technique was improved and applied to experiments where low energy hydrogen isotopes were used [1,9]. In those experiments, using high fluences of low energy deuterium, molecular deuterium was detected at depths greater than 450 nm.

The intent of the work reported here was to detect the type of defect in tungsten that is responsible for the molecular retention. High purity tungsten samples were exposed in the PISCES facility at the University of California, San Diego to high fluences of 100 eV deuterium. Transmission electron microscopy at Sandia National Laboratories and at Ohio State University was used to examine the tungsten microstructure after the plasma exposure.

2. Experimental

The tungsten used in these experiments was provided by Plansee Aktiengesellschaft. It is a powder metallurgy product with a purity of 99.99%. Prior to plasma exposure, the samples were polished and then annealed in vacuum for one hour at 1273 K. The sample was exposed to deuterium plasma in the PISCES facility at the University of California, San Diego. The plasma exposure

---

[*] Corresponding author.
E-mail addresses: causey@sandia.gov (R.A. Causey), rkolasi@sandia.gov (R.D. Kolasinski).

0022-3115/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2009.01.300

was 100 eV deuterons at a flux of 2.5×10^{22} D/m^2 s and 573 K for 5100 s for a fluence of 1.27×10^{26} D/m^2.

Samples were prepared for TEM observation using the Focused Ion Beam (FIB) method. After depositing a Pt protective layer over the region of interest, a 20 μm by 8 μm by 2 μm slice was trenched from each sample using an FEI Dual Beam Nova 600 or Helios Nanolab. Damage due to milling at 30 KV was removed using a Fischione 1040 Nanomill at less than 1 KV. This allowed examination of the microstructure immediately below the exposed surface to a depth of about 5 μm. Examination of the microstructure was done on a JEOL 1200 EX, JEOL 2010 or FEI Titan TEM.

3. Results

The as-received warm rolled material contained elongated grains about 0.5 μm wide by 1 μm long. The TEM results for the sample exposed to a fluence of 1.27×10^{26} D/m^2 for 5100 s is shown in Fig. 1(a) and (b). Fig. 1(a) is an area 3 to 5 μm below the surface, Fig. 1(b) is just below the exposed surface. No evidence of either nano-bubbles or large voids from nano-bubble coalescence was observed. The mottled contrast may be from ion-milling damage, although special efforts using successively lower KV FIB milling followed by Ar nano-milling were used to minimize or eliminate ion-milling damage. The sample, while annealed before exposure, is believed to still contain some defect structure from warm-rolling. The structure has some similarities to that reported by Trybus et al. [22], but none of the typical cellular nature of the structure reported there were found in the present samples. In the work of Alimov et al. [9], deuterium concentrations on the level of 0.2% (2000 appm) were detected almost 0.5 microns into the sample. Additionally, the slope of the concentration as a function of depth into the sample did not suggest that the concentration was rapidly dropping at that depth. With the resolution used in this study, nano or micro bubbles or voids containing that much deuterium should have been seen.

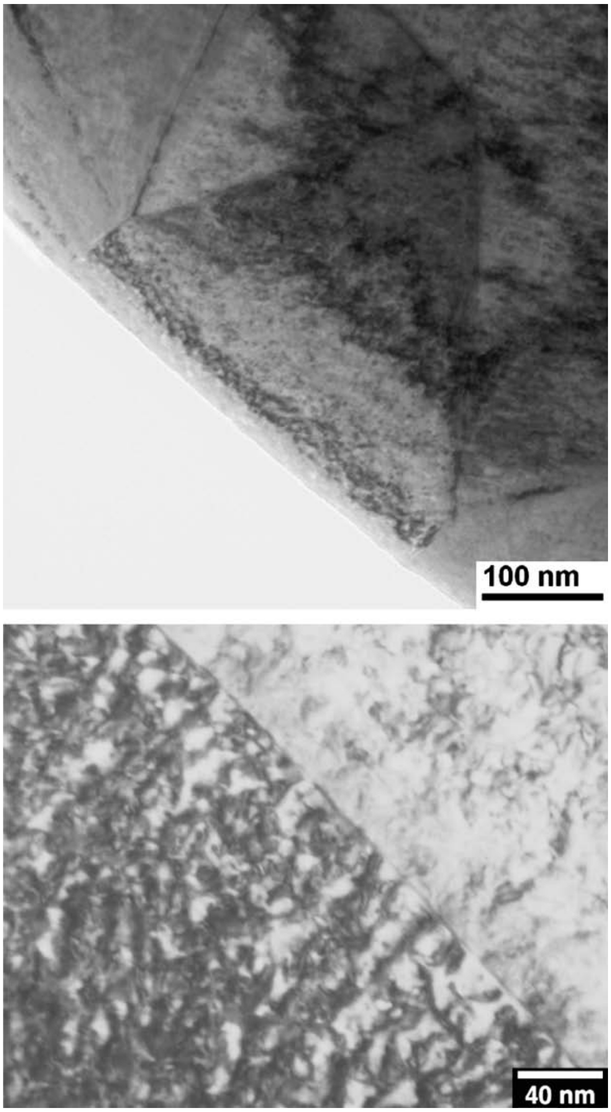

Fig. 1. (a) Area 3–5 mm below the surface exposed to the plasma; (b) close-up of near-surface region indicating that neither nano-bubbles nor large bubbles were observed.

Based on these negative findings, we considered other potential locations for molecular hydrogen within the material. While the samples used in this study showed extensive blistering as have almost all those in other studies [13–19], blisters were not initially considered. The work of Alimov et al. [9] showed the integrated deuterium concentration to be fairly uniform. While the integrated deuterium concentration in the Alimov et al. [9] sample may have been continuous, closer examination of the results showed the concentration to be dominated by discrete ‘bursts’ of gas. For the single crystal sample used in that low energy experiment, the signal as recorded by the residual gas analyzer showed approximately 50 to 80 discrete bursts. Even more revealing were the SIMS results for the samples used in the higher energy study [21]. For the three samples exposed at different temperatures, the sizes of the bursts appeared to scale very closely with the size of the blisters. It is contended that these bursts actually represent the SIMS beam breaking through the different thickness blister caps. The smoothness of the integrated concentration profile is due to the large area over which the SIMS beam is rastered.

The statement that molecular deuterium exists in the blisters is not intended to imply that the blisters were formed by the coalescence of gas filled bubbles. It is far more likely that these blisters resulted from integrated lateral stress from trapped deuterium in the first several microns of the surface layer [23]. Without preexisting voids or vacancy agglomeration typical of higher energy implantation to serve as nucleation sites for growth, the lateral stress model is more the logical explanation for the blistering. The accumulation of the deuterium in the blisters likely occurred after the blister formation.

For the concept of molecular hydrogen isotope retention in the blister voids to be valid, modeling of hydrogen isotope retention and release from blisters should agree with past experimental results. To model the results, an understanding of the hydrogen induced blisters on tungsten is required. Alimov et al. [9] reported blisters with diameters between 2 and 50 μm on both single crystal and polycrystalline samples after exposure to 2×10^{24} D/m^2 at 200 eV. At 920 K with 90 eV ions, Ye et al. [16] reported blisters to increase in size with increasing fluence, reaching 200 μm at 4.7×10^{25} D/m^2. For polycrystalline samples exposed at 7 to 98 eV deuterons, blisters with diameters of 0.1–2 μm were seen. For the large blisters, a blister cap of 0.4 μm thickness was measured. Wang et al. [15] saw the blister size increase as the energy of the exposure was increased from 100 eV up to 200 eV and 1 KeV. There was a corresponding decrease in blister density with the energy increase. For a hydrogen ion energy of 333 eV and a fluence of 1×10^{25} H/m^2, Ueda et al. [18] saw spherical blisters with sizes from 5 to 210 μm and a number density of 450 blisters/mm^2. Their measurements showed the blister cap to have a thickness about one order of magnitude smaller than the diameter. The cumulative evidence from the references would suggest blister caps to vary from less than 0.1 μm up to about 20 μm.

For modeling purposes, we considered recent thermal desorption spectroscopy results from a series of tests performed in the Tritium Plasma Experiment (TPE) [24]. In this study, PLANSEE W samples were exposed to a 70 eV flux of 1.1×10^{22} D/m^2 s for approximately 2 h. The TDS spectra obtained after a series of exposures revealed several distinct desorption peaks, depending on the sample temperature. For this particular calculation, we consider an exposure at a temperature of 623 K, as mentioned in Ref. [24]. Posttest optical microscope images of the sample in Fig. 2 show a population of blisters ranging in size from less than 10 μm up to 50 μm in diameter, with a sizeable fraction of the surface covered.

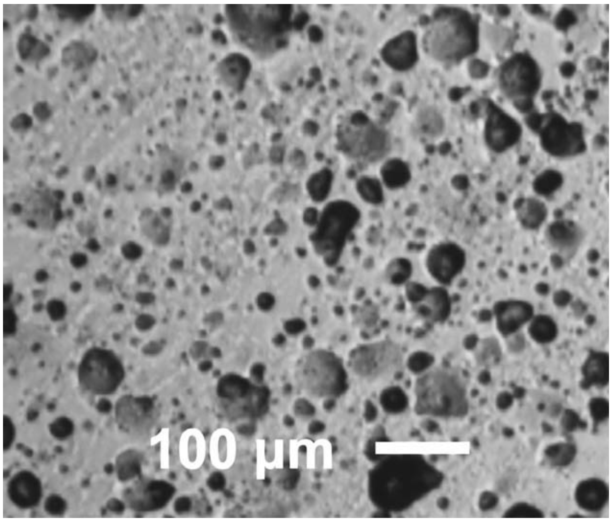

Fig. 2. Optical microscope image showing blistering on the surface of a PLANSEE W sample exposed in the tritium plasma experiment. Exposure conditions were: flux: 1.1×10^{22} m^{-2} s^{-1}; fluence: 8.1×10^{25} m^{-2}; $T_{sample} = 623$ K (image from Ref. [24]).

The experimental TDS spectrum (shown in Fig. 3) is dominated by a desorption peak centered at 775 K, although peaks at $T = 650$ K and 1100 K are more prominent at other exposure temperatures. Most existing codes (such as DIFFUSE and TMAP) only allow for atomic trapping. Hence, the conventional procedure for modeling this TDS spectrum would be to vary the trap energy and concentration to match the desorption temperature and peak height, respectively. To demonstrate this, we used the TMAP7 [25] computer code to predict the thermal desorption spectra for the lower temperature sample based solely on atomic trapping. The diffusivity and solubility given by Frauenfelder [26] were assumed. Including 1.3 eV traps at a concentration of 200 appm allowed us to obtain the fit shown in Fig. 3, reproducing the peak at 775 K. While this provides a satisfying fit to the experimental data, it is questionable whether this method is accurately modeling the release of H from more complex structures on the surface (such as blisters.)

We considered an alternate approach to model D release from blisters, which includes an enclosure of finite volume located with-

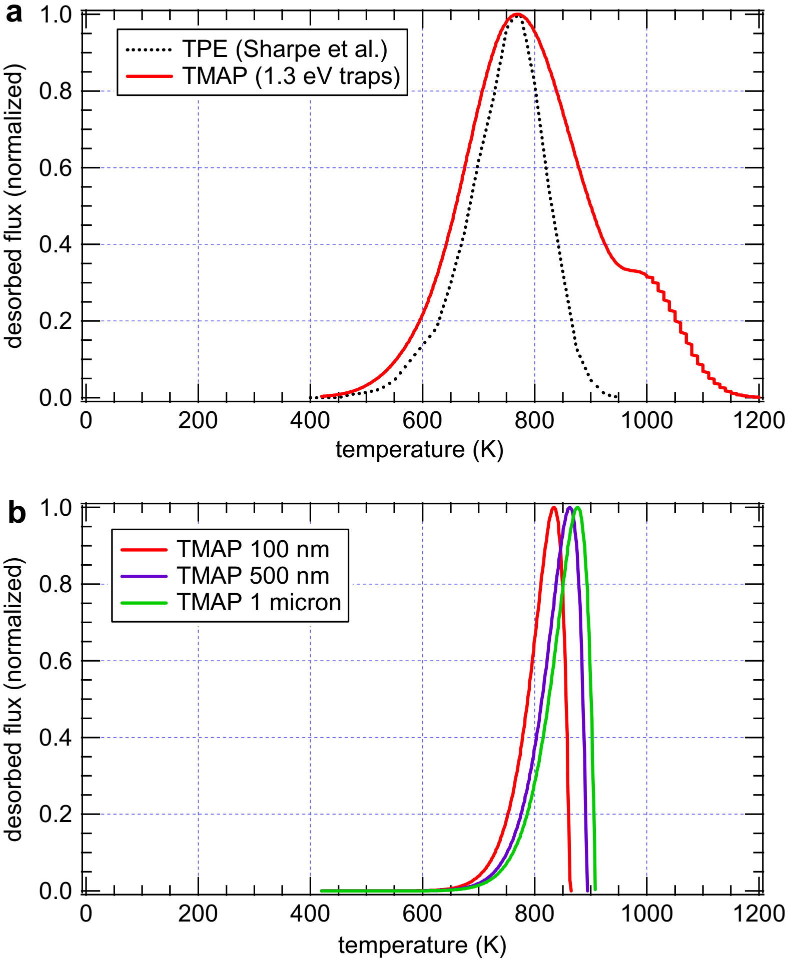

Fig. 3. (a) TMAP7 code fit to TPE thermal desorption spectra (data from Ref. [24], assuming atomic trapping with 1.3 eV traps at a concentration of 200 appm; (b) TMAP7 code fit assuming molecular retention under blister caps (ranging from 100 nm–1 μm in thick).

in the irradiated surface. With this type of configuration, a pressure of H gas can be accumulated in the enclosure during irradiation and depleted during thermal desorption. Significant geometrical simplifications were necessary to implement this type of model in TMAP, given its ability to accommodate diffusion in one dimension only. However, our goal here is a 'proof of concept' simulation which can show how blisters can contribute to TDS spectra. Shown in Fig. 3 are the TMAP7 results for gas release from blisters (enclosures) with blister cap thicknesses of 0.1, 0.5, and 1.0 microns thick. The results are centered about 50–100 K above the main peak of the thermal desorption spectra with the 0.1 μm thickness coming closest to the experimental data. The discrepancy between the experimental results and the modeling results should not be interpreted to suggest that the blister caps are less than 0.1 μm thick. There are possible errors in both the thermal desorption data and the hydrogen transport data from Frauenfelder [26] that could easily explain the difference. Furthermore, the simplifying assumptions in the model also likely contribute to this difference. However, these results do suggest that the release of H from blisters could be a contributing factor to the TDS spectrum shown above.

The analysis above could be enhanced by including a distribution of blister sizes from SEM images or profilometry traces to the TDS spectrum. A more precise treatment is prevented by the limitations of diffusion codes presently in use within the fusion community. The ability to account for complex geometries on the plasma facing surface (as well as a more sophisticated treatment of trapping within the bulk) would be required for this purpose.

4. Discussion

From a tritium inventory point of view, the fact that the molecular hydrogen seen in tungsten after low energy implantation is in blisters is good news. Blisters are limited to the surface region and are likely to rupture when stresses in the material become high. As a result, they will release their inventory and the contribution to total tritium retention from this molecular component is quite limited. The presence of blisters would also shield areas deeper in the material by preventing the atoms migrating further inward (given the low solubility of W).

On the other hand, blistering will enhance erosion. Once a blister has formed, the volume below the blister cap begins to accumulate hydrogen. The eventual pressure in that volume can become extremely high. Rather than reach such extreme pressures, the blister cap effectively fails, venting the gas to the area above the tungsten. Whether the blister has vented or not, the thermal contact with the substrate below has been lost. Even if the blister can survive normal conditions, then power excursions such as ELMs and disruptions will eventually melt or vaporize the thin blister cap and result in elevated erosion.

5. Summary

Based on earlier experimental results that showed tungsten samples exposed to high fluences of low energy hydrogen plasmas to contain molecular hydrogen, transmission electron microscopy was employed to look for evidence of bubbles in such samples. The microscopy work did not find any such bubbles. Reexamination of past results suggests the molecular hydrogen to reside in blisters located on the sample surface. It is likely that the hydrogen permeates into the blister volume after formation, and is not the cause of the blisters. Modeling of hydrogen release from these voids agrees fairly well with past experimental data. The accumulation and release of H in blisters could serve to mitigate inventory issues in ITER, although more study is needed to understand these processes, especially in a mixed material environment.

References

[1] V.K. Alimov, J. Roth, Phys. Scr. T128 (2007) 6.
[2] A.P. Zakharov et al., J. Nucl. Mater. 241–243 (1997) 52.
[3] O.V. Ogorodnikova, J. Roth, M. Mayer, J. Appl. Phys. 103 (2008).
[4] R.A. Causey, J. Nucl. Mater. 300 (2002) 91.
[5] G. Garcia-Rosales et al., J. Nucl. Mater. 233–237 (1996) 803.
[6] P. Franzen et al., J. Nucl. Mater. 233–237 (1996) 1082.
[7] R.A. Causey et al., J. Nucl. Mater. 266–269 (1999) 467.
[8] T.J. Venhaus, R.A. Causey, Fus. Technol. 39 (2001) 868.
[9] V.K. Alimov et al., J. Nucl. Mater. 375 (2008) 192.
[10] A. van Veen et al., J. Nucl. Mater. 155–157 (1988) 1113.
[11] H. Eleveld, A. van Veen, J. Nucl. Mater. 191–194 (1992) 433.
[12] H. Eleveld, A. van Veen, J. Nucl. Mater. 212–215 (1994) 1421.
[13] A.A. Haasz et al., J. Nucl. Mater. 266–269 (1999) 520.
[14] F.C. Sze et al., J. Nucl.Mater. 264 (1999) 89.
[15] W. Wang et al., J. Nucl. Mater. 299 (2001) 124.
[16] M.Y. Ye et al., J. Nucl. Mater. 313–316 (2003) 72.
[17] T. Shimada et al., Fus. Eng. Design 66–68 (2003) 247.
[18] Y. Ueda et al., J. Nucl. Mater. 337–339 (2005) 1010.
[19] W.M. Shu et al., J. Nucl. Mater. 367–370 (2007) 1463.
[20] V.K. Alimov et al., J. Nucl. Mater. 290–293 (2001) 389.
[21] V.K. Alimov et al., Phys. Scr. T108 (2004) 46.
[22] C.L. Trybus, C.H. Sellers, R.A. Anderl, in: Proceedings of the TMS Symposium: Tungsten and Tungsten Alloys, Recent Advances, 1991.
[23] E.P. EerNisse, S.T. Picraux, J. Appl. Phys. 48 (1977) 9.
[24] J.P. Sharpe, R.D. Kolasinski, M. Shimada, R.A. Causey, J. Nucl. Mater. 390–391 (2009) 709.
[25] G.R. Longhurst, J. Ambrosec, Fus. Sci. Technol. 48 (2005) 468.
[26] R. Frauenfelder, J. Vac. Sci. Technol. 6 (3) (1969) 388.