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Deuterium retention in W, W1%La, C-coated W and W_2C ☆

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Abstract

This paper reports the results of a systematic investigation into retention of deuterium implanted into various forms of W including: reduction-rolled, powder-metallurgy foil; discs of W1%La alloy; W and W_2C prepared by chemical vapor deposition (CVD) and annealed C-coated W discs. Deuterium was implanted at energies of 0.5 keV/D with fluxes of $\sim 3 \times 10^{19}$ D/m^2 s and fluences of 3×10^{23} D/m^2, for samples at temperatures from 23°C to 400°C. Retained deuterium quantities were measured using thermal desorption spectroscopy (TDS). Retention in annealed CVD-W and W1%La, for implantation temperatures less than 200°C, is below that in annealed W foil, indicating that trapping may be affected by the different material defect structures. For implantation temperatures less than 300°C, retention in CVD-W_2C is somewhat higher than that in CVD-W, indicating trapping could be enhanced by trace carbon impurities, differences in W_2C material structure and recoil carbon-induced material damage. Implantation into C-coated W resulted in orders of magnitude more retention than in uncoated material, because of trapping in the carbon coating. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Divertor material; Hydrogen; Ion irradiation; Tungsten; Carbon

1. Introduction

Tungsten and carbon are materials selected for plasma-facing components (PFCs) exposed to high heat fluxes in fusion devices. Tritium uptake and retention in tungsten used in a mixed-material fusion device (W and C PFCs) has been difficult to predict accurately because of inadequate understanding of trapping in tungsten and in complex W–C material layers that may form on PFC surfaces of a mixed-material fusion system. This information is relevant to safety assessments of advanced fusion systems.

The purpose of this paper is to present the results of a systematic investigation into retention of deuterium in various forms of W: reduction-rolled, powder-metallurgy foil; discs of W1%La alloy; W and W_2C prepared by chemical vapor deposition (CVD), and annealed C-coated W discs. The emphasis is on thermal desorption spectroscopy (TDS) measurements for implanted samples to quantify deuterium retention as a function of implantation temperature and to investigate the influence of material defects and carbon impurities on trapped deuterium concentrations for the different materials.

This work complements much research that has been reported recently to further an understanding of tritium uptake and retention in pure W and complex W materials. Previous studies, using hydrogen isotope implantation coupled with permeation experiments [1], TDS experiments [2–13], ion-beam analyses [14,15] and perturbed angular correlation experiments [16], have investigated the following: retention and release behavior, saturation effects, implantation fluence and temperature dependence, material structure dependence and the influence of bulk and surface defects and carbon. General results indicate the following: implanted deuterium is trapped with nominal energies of 0.5 eV (surface defects), 1.2–1.5 eV (ion-induced damage and intrinsic bulk defects) and 2–4 eV (chemical binding to C). Hydrogen isotopes retained in such traps exhibit TDS peaks with nominal temperatures of 130°C, 230–330°C,

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430–530°C and 630–930°C, with some variation in peak temperatures dependent on the experiment heating rate and the release depth for the hydrogen. Frauenfelder's [17] diffusivity and solubility are consistent with some experiments [1] but not tested in most TDS studies, and evidence for deep transport and trapping of hydrogen beyond the implantation zone has been observed [4,11]. A general overview of tungsten use for fusion is given by Yoshida [18].

2. Experimental details

All specimens were 16.5 mm in diameter with thickness of 25 μm for W foil, 0.5 mm for W1%La and 0.75 mm for CVD-W and CVD-W_2C products. Tungsten foil samples were punched from high purity foil (99.95% W by weight), a reduction-rolled, powder-metallurgy product with principal chemical impurities: O (340), C (460), N (130), H (920), Fe (160), Mo (570), Ca (140), Na (160), P (300), Si (200) and others (320) on an atomic parts per million (appm) basis. Foils were implanted 'as-received' and after annealing at 1200°C. The 0.5-mm W1%La disc samples, the alloy grade proposed for ITER by PLANSEE, were polished to a mirror finish and annealed at 1000°C prior to implantation.

Tungsten and tungsten carbide samples, made using proprietary CVD techniques by ULTRAMET, were machined from deposits collected on Mo cylindrical mandrels exposed to different CVD atmospheres. CVD-W material was deposited in a single deposition cycle, whereas, multiple cycles were required to achieve the required thickness for CVD-W_2C. As a consequence, the CVD-W_2C microstructure contained distinct columnar layers and interfaces between the layers. The CVD-W, with a columnar microstructure and no indications of porosity or secondary-phase interstitials, had a density of 19 g/cm^3 and a microhardness of 525 VHN. As determined by XRD measurements, the CVD tungsten carbide was principally W_2C with indications of trace C, most likely at the grain boundaries of the structure. CVD-W_2C had a density of 18.3 g/cm^3 and a microhardness of 2040–2450 VHN, dependent on the sample tested. Prior to deuterium implantation, the discs were polished to a mirror finish and annealed at 500°C or 1000°C.

C-coated samples were prepared by exposing polished W1%La discs to carbon vapor generated from an arc between two carbon electrodes in a vacuum system. Nominal coating thickness ranged from 1000 to 1500 Å. C-coated samples with 1000 Å thickness were used in annealing studies to determine inter-diffusion properties of the C–W system. Depth-profile Auger analysis of three different samples heated to 400°C, 600°C and 800°C for 3 h each revealed that some inter-mixing was observed at the C–W interface for the sample annealed at 800°C. No inter-mixing was observed in the other samples.

Deuterium implantation of the test samples was done with a system that delivered 1.5 keV D_3^+ ions (500 eV/D) through a 0.2-cm^2 beam-defining aperture in front of the sample. Typical flux densities were 3×10^{19} D/m^2 s, and specimens were exposed to a fluence of about 3×10^{23} D/m^2. A Faraday cup was used to measure the beam current through the aperture. The disc samples were mounted on a holder that could be attached to a linear translator for installation on a heater fixture in the target chamber. Samples were heated radiantly and temperatures were measured with a contacting thermocouple. Base pressure of the target chamber was 5×10^{-9} Torr.

Measurements of deuterium retained in the implanted samples were made with a vacuum TDS system equipped with a fast-response radiant tube furnace surrounding a quartz vacuum chamber. A quadrupole mass spectrometer (QMS) was used to measure gases released during sample heating (30°C/min linear ramp from 25°C to 1000°C). QMS calibration was done with deuterium standard leaks. Our approach required air-transfer of a sample from the ion-beam system to the TDS system. QMS measurements indicated this transfer resulted in generation of higher hydrogen concentrations during a TDS experiment, with consequent formation of HD and interfering H_3, both of which were accounted for in the analysis.

3. Measurements and results

In this section, we summarize the results of the TDS measurements to determine the release behavior and the quantities of deuterium that were retained in the samples after implantation. Delay times from end of implantation to initiation of TDS measurement ranged from 2 h to several days, however we tried to maintain consistency with a material measurement series. Although no systematic studies were made to evaluate the influence of delay times on deuterium retention, this issue was checked by means of multiple experiments at 200°C implantation and different delay times for a W_2C sample, and the retention results agreed within the uncertainties of our measurements. For these experiments, we used QMS masses 3, 4 and 20 as signatures for HD, D_2 and CD_4. To accurately determine the HD component at high TDS temperatures, we had to estimate the H_3 interference resulting from a growing H_2 concentration in the TDS system. The HD calibration factor was assumed to be the same as that for D_2. The calibration factor for the CD_4 data was estimated from the D_2 calibration data by applying a sensitivity factor derived from the relative ionization coefficients. Based on the uncertainties in the D_2 standard leaks and in the method used to estimate the CD_4 calibration, we expect absolute uncertainties in the derived gas quantities to be about 25% for HD and D_2 and 50% for CD_4.

Summary results from the TDS measurements for W foil, W1%La and CVD material are presented in Figs. 1–4. The results are plotted as absolute release rates in units of D/min as a function of elapsed time, with the temperature ramp plotted against the right axis. In all cases the spectra are the sum of HD and D_2. Fig. 1 compares TDS spectra for three unannealed 25-μm W foil samples that were implanted at 100°C, 200°C and 300°C. Desorption peaks are identified at nominal temperatures of 140°C, 300°C, 400°C and 500°C. Fig. 2 compares TDS spectra for three 25-μm W foil samples, annealed at 1200°C and then implanted at 100°C, 200°C and 300°C. Desorption peaks are identified at nominal temperatures of 300°C, 400°C and 570°C. TDS spectra for CVD-W-sample 3 implanted at 100°C, 200°C, 300°C and 400°C are shown in Fig. 3. Desorption peaks are identified at nominal temperatures of 200°C, 430°C and 530°C, with a weak peak at 725°C. Results from TDS experiments for one of the CVD-W_2C samples implanted at 27°C, 100°C, 200°C and 300°C are shown in Fig. 4. Desorption peaks are identified at nominal temperatures of 270°C, 320°C, 400°C and 560°C, with a weak peak at 750°C. Although TDS spectra for the experiments on W1%La and C-coated W1%La are not shown here, the spectra for W1%La are similar to those for annealed W foil, and the spectra for C-coated W1%La had a CD_4 release peak at 525°C and a D_2 release peak at 750°C, as expected for release from an implanted carbon layer.

Retention data derived from the measured TDS spectra are presented in Fig. 5 as areal densities (D/m^2) along with estimates of trapped concentrations from permeation experiments [1] that were made for unannealed and annealed W foils. Lines are not analytical fits, but they are meant to guide the eye to show comparative trends. The only data set that does not have an associated line is that for the unannealed W foil, with one of three data points identified at 200°C.

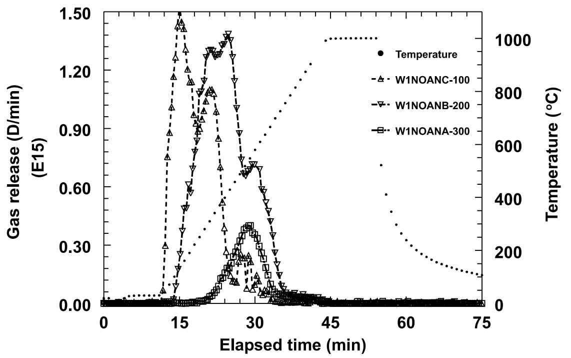

Fig. 1. TDS spectra for unannealed 25-μm W foils implanted at 100°C, 200°C and 300°C.

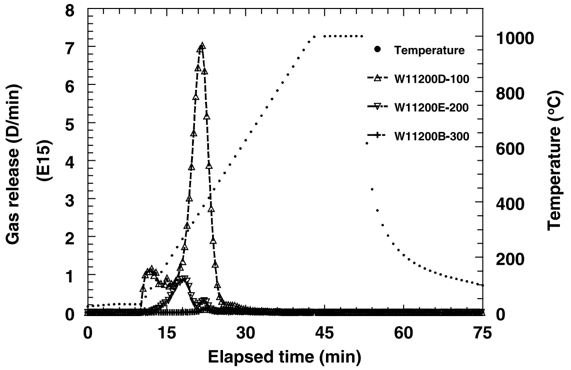

Fig. 2. TDS spectra for 25-μm W foils annealed at 1200°C and implanted at 100°C, 200°C and 300°C.

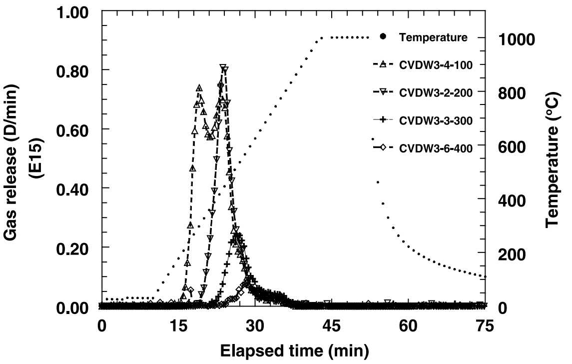

Fig. 3. TDS spectra for CVD-W sample 3 (0.75 mm thick) that was implanted at 100°C, 200°C, 300°C and 400°C.

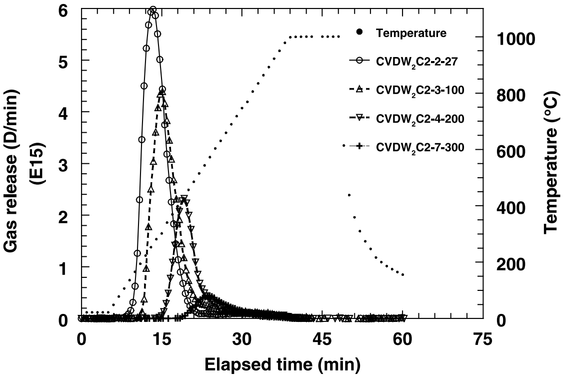

Fig. 4. TDS spectra for CVD-W_2C sample 2 (0.75 mm thick) that was implanted at 27°C, 100°C, 200°C and 300°C.

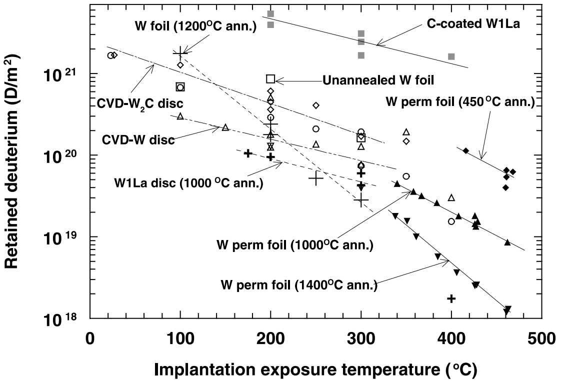

Fig. 5. Comparison of deuterium retention data obtained from current TDS experiments and from previous permeation experiments for the 25-μm W foils [1].

4. Discussion and conclusions

This work entailed a systematic study of deuterium retention in various forms of W using deuterium implantation and TDS. The results indicate that retention of implanted deuterium is dependent on implantation temperature, material type and structure, prior heat treatment and the presence of surface and bulk carbon.

As shown in Fig. 5, retention in CVD-W and W1%La is significantly below that in tungsten foil, especially for implantation temperatures less than 200°C. This could be due to the heavily defected microstructure produced in the reduction-rolling process for the thin foil. Above, 200°C, however, the TDS results indicate the opposite trend, possibly because of diffusive transport and deeper bulk trapping in the thicker CVD-W and W1%La samples. As we observed in earlier work [1], annealing of the thin tungsten foil had a dramatic impact on trapping of implanted deuterium. Results from those implantation/permeation studies for foil annealed at 1400°C agree well with extrapolated TDS retention for foils annealed at 1200°C. For comparable fluences and an implantation temperature of 200°C, the absolute retention results for W are in fair agreement with those by Haasz et al. [8].

For implantation temperatures below 300°C, the results in Fig. 5 indicate that retention in CVD-W_2C is somewhat higher ($\sim$2 times) than retention in CVD-W. We suspect that trapping is enhanced in the W_2C because of trace C impurities in the bulk and small differences in the microstructure (multilayers and interfacial impurities). In addition, beam-induced damage is higher in the W_2C material because recoiling C atoms have sufficient energy and momentum to dislodge a W atom from its lattice, whereas 500-eV D does not.

With the exception of the C-coated W material, TDS peaks were observed at similar temperatures for various forms of W, though the relative magnitudes of the TDS structure varied from material to material. This indicates similar trapping sites but different trap concentrations in the various materials. Based on the measured TDS spectra, we observe desorption at primarily four temperatures: 130°C, 300°C, 400°C and 530°C, with a weak peak at 725°C in some cases. Although the correspondence is not exact for all material spectra, the largest deviations from these values are at higher implantation temperatures, a condition that could result in deeper transport of the implanted deuterium and an upward shift in the desorption peak temperature. Desorption peaks identified in our TDS spectra are in excellent agreement with those observed in the previous works [2–13], providing evidence of trapping at surface, intrinsic and ion-induced defect sites and chemical binding to carbon.

Finally, we have shown that C-coated tungsten results in retention that is orders of magnitude greater than that in a pure tungsten surface, because of trapping in the carbon. Annealing studies for C-coated tungsten indicate little inter-diffusion of C and W for temperatures less than 800°C. Consequently, retention in carbon-covered tungsten components is dominated by uptake in the carbon, a result that was demonstrated by Schleussner et al. [11] and Sze [12] for tungsten exposed to plasmas with carbon impurities.

References

[1] R.A. Anderl et al., Fus. Technol. 21 (1992) 745.
[2] H. Eleveld et al., in: Proceedings of the 16th Symposium On Fusion Technology, SOFT, London, 1990, p. 376.
[3] H. Eleveld, A. van Veen, J. Nucl. Mater. 191–194 (1992) 433.
[4] V.K. Alimov, B.M. Scherzer, J. Nucl. Mater. 240 (1996) 75.
[5] P. Fransen et al., J. Nucl. Mater. 241–243 (1997) 1012.
[6] J.W. Davis, A.A. Haasz, J. Nucl. Mater. 223 (1995) 312.
[7] A.A. Haasz, J.W. Davis, J. Nucl. Mater. 241–243 (1997) 1076–1081.
[8] A.A. Haasz et al., J. Nucl. Mater. 258–263 (1998) 889.
[9] A.A. Haasz et al., J. Nucl. Mater. 266–269 (1999) 520.
[10] R. Causey et al., J. Nucl. Mater. 266–269 (1999) 467.
[11] D. Schleussner et al., J. Nucl. Mater. 266–269 (1999) 1296.
[12] F.C. Sze, J. Nucl. Mater. 266–269 (1999) 1212.
[13] M. Poon et al., J. Nucl. Mater 283–287 (2000) 1062.
[14] S. Nagata et al., J. Nucl. Mater. 266–269 (1999) 1151.
[15] T. Horikawa et al., J. Nucl. Mater. 266–269 (1999) 1091.
[16] J.R. Fransens et al., J. Phys.: Condens. Matter 3 (1991) 9871.
[17] R. Frauenfelder, J. Vacuum, Sci. Technol. (1969) 388.
[18] N. Yoshida, J. Nucl. Mater. 266–269 (1999) 197.