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Behavior of tungsten exposed to high fluences of low energy hydrogen isotopes

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Abstract

Tungsten is a candidate plasma facing material under investigation in a Sandia National Laboratories project conducted at Los Alamos National Laboratory. Samples of 99.95% tungsten provided by Plansee Aktiengesellschaft were exposed to 100 eV deuterium and tritium ions at a range of fluxes from 2.3×10^{17} to 1.3×10^{18} ions/cm^2 s for one hour at 623 K in the tritium plasma experiment. The samples were outgassed to determine the amount of retained hydrogen isotopes. The retention scaled at slightly greater than the square root of the fluence. The fractional retention was on the order of 10^{-5}. The data from these experiments were combined with previous results to construct a comprehensive model of the migration and retention behavior for hydrogen in tungsten. A second set of experiments involved exposing 99.95% tungsten foils provided by ÆSAR to 100 eV deuterons at a flux of 6×10^{17} D/cm^2 s for 30 min at 423 and 373 K. Scanning Electron Microscopy analysis was performed on the samples to determine the effects of the plasma exposure. Unannealed samples revealed extensive blistering with many blister caps removed. Samples annealed to 1473 K showed minor blistering, and samples annealed to 1273 K showed no blistering. The SEM analysis was used in conjunction with the retention results to understand the role of annealing and defects in trapping within the tungsten. © 2001 Published by Elsevier Science B.V.

Keywords: Tungsten; Tritium inventory

1. Introduction

Tungsten and tungsten alloys are candidate plasma facing components for fusion machines due to their excellent thermal properties, low sputtering coefficients, and low solubility for hydrogen. This report describes the retention behavior and surface response of tungsten samples bombarded by high fluxes of hydrogen isotopes at a range of temperatures. The experiments were performed in the tritium plasma experiment (TPE) at Los Alamos National Laboratory.

The reader is referred to the article by Causey and Venhaus [1] for a complete literature review on the behavior of plasma-driven hydrogen in tungsten. The purpose of the present work is to employ the current theories of hydrogen behavior in tungsten, with the generally accepted tungsten material parameters, in a finite-difference calculation describing several experimental data sets. Part I of the present study will concentrate on previous and current experimental retention measurements of 100 eV hydrogen isotopes in 99.95% pure tungsten samples exposed for various temperatures and fluxes in the TPE at Los Alamos National Laboratory. Simulations performed with the Tritium Migration Analysis Program (TMAP4) developed at INEEL [2] will be presented. Part II will present SEM analysis of plasma exposed tungsten surfaces and a discussion of near-surface mechanisms believed to be important in the trapping behavior.

2. Experimental procedures

Plansee Aktiengesellschaft provided the 2-mm thick powder metallurgy samples used in these experiments.

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Table 1
Sample designation and parameters used in the experiments

Sample name	Material	Anneal temp. (K)	Flux (ions/cm^2 s)	Fluence (ions/cm^2)	Sample temp. (K)	Analysis
WW-2	Plansee	1273	1.2×10^{18}	4.3×10^{21}	423	NRA [4]
WW-3			3.1×10^{18}	1.1×10^{22}	573	
WW-8	Plansee	1273	8.7×10^{17}	3.1×10^{21}	423	TDS [4]
WW-9					573	
WW-10					723	
WW-11					973	
W-15	Plansee	1273	2.3×10^{17}	8.3×10^{20}	623	TDS
W-16			4.6×10^{17}	1.7×10^{21}		
W-17			1.3×10^{18}	4.7×10^{21}		
F-12	ÆSAR foil	–	6.8×10^{17}	1.2×10^{21}	423	SEM
F-17		1273				
F-18		1473				
W-19	Plansee	1273	6.8×10^{17}	1.2×10^{21}	373	

The pure tungsten samples were polished after the annealing. The disks were 50.8 mm in diameter, and 2 mm thick. ÆSAR provided the 50 μm powder metallurgy tungsten foil samples. The foils were produced by a powder metallurgy process, rolled to achieve the correct thickness, then heat treated to relieve stress. The purity of all samples is 99.95%. After receipt, the samples were annealed for one hour in an inert atmosphere at the temperatures shown in Table 1. One of the ÆSAR foil samples was not annealed.

All experiments were performed in the TPE, an arc-reflex type plasma source. This device is described elsewhere [3]. The working gas consisted of 97% deuterium and 3% tritium, and was fed to the system at a flow rate of 30 atm cm^3/min. The acceleration energy for the deuterons and tritons was provided by a negative bias of 100 V applied to the sample. The primary impurity in the system was water vapor at 1.5×10^{-5} Pa. The flux, exposure time, and exposure temperature for all experiments is shown in Table 1. The plasma provided the heating of the samples. A copper disk behind the sample provided an even heat distribution. By varying the thickness and composition of a third disk (the one in contact with a water-cooled holder), different sample temperatures could be obtained.

Samples exposed to a tritiated plasma were transferred in air to an outgassing system. The temperature of the sample was ramped at a rate of 20 K/min to a final temperature of 1473 K. Gas consisting of 99% argon and 1% hydrogen was swept over the sample and through an ionization chamber that monitored the tritium concentration. Total isotope retention was calculated by the flow rate ratio. In samples used in SEM analysis and nuclear-reaction profiling, a pure deuterium plasma was used.

3. Results and discussion

3.1. Retention vs. temperature

3.1.1. Results

In a previously reported experiment [4], samples WW-8, WW-9, and WW-10, and WW-11 were exposed to a flux of 8.7×10^{17} ions/cm^2 s for one hour at the temperatures shown in Table 1. The retention values are shown in Fig. 1. A recently obtained estimated data point has been added to this set, and is noted in the figure. This point was estimated from the flux-dependent retention data at 623 K in Fig. 2; for a retention value of 5×10^{16} (D + T)/cm^2 the corresponding flux is ~$8.7 \times$

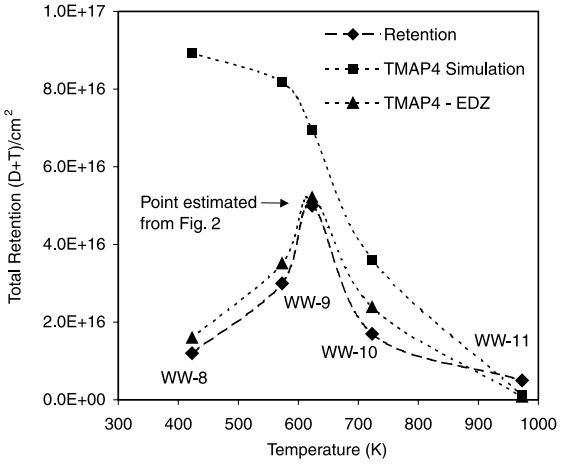

Fig. 1. Experimental retention results (◆), TMAP4 simulation using best-fit parameters (■), and TMAP4 retention results using $C_0 = 0$ and enhanced diffusion in the implant zone (▲).

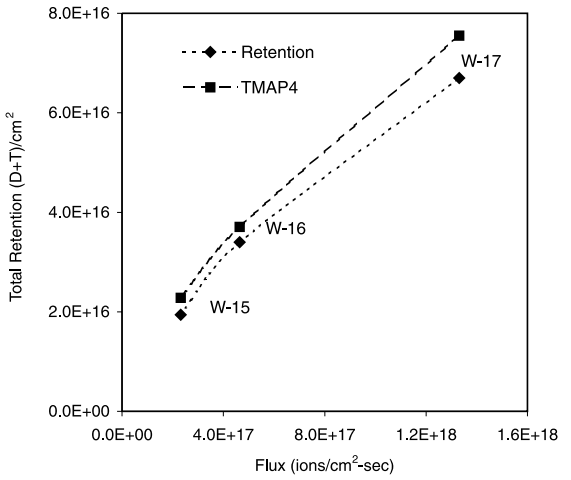

Fig. 2. Experimental (◆) and simulated (■) retention values for samples exposed at a constant temperature of 623 K and a range of fluxes for one hour. Lines are drawn to guide the eye.

10^{17} ions/cm^2 s. The experimental retention values shown in Fig. 1 are low at low and high temperatures, with a maximum in retention at about 623 K.

3.1.2. Modeling

Model parameters were taken from literature. The diffusivity is given by Frauenfelder [5] as 4.1×10^{-7} exp(-0.39 eV/kT) m^2/s. The recombination coefficient was reported by Anderl et al. [6] as $k_r = 3.2 \times 10^{-15}$ exp(-1.16 eV/kT) m^4/s. It is believe that the intense hydrogen bombardment from the TPE plasma quickly reduces any oxides on the surface, and provides a near-surface 'agitation' to stimulate the release. Therefore, the case for an infinitely high recombination coefficient (i.e., $C_0 = 0$) was also considered. Using a trap concentration of 400 appm, as determined by NRA analysis [4], and a trap energy of 1.3 eV, yielded the best fit to the retention values for the high temperature data. The TMAP4 simulated retention values are shown in Fig. 1 along with the experimental data.

The simulated retention results follow the experimental results at high temperatures; however, the model fails at the lower temperatures. For the $C_0 = 0$ case, the release rate is governed by the diffusivity. However, the diffusivity always decreases as the temperature decreases, which would increase retention. There are two possible explanations for the enhanced release at lower temperatures. One is a modification of the surface. This possibility is discussed later in Section 3.3.2. The other possibility is an 'agitation' of the near-surface solute atoms by the incoming flux. One has to remember that a flux on the order of 10^{17} ions/cm^2 s is being implanted to a depth of only a few nm. This effect could be termed ion induced desorption. Whatever the cause, the effect can be simulated by increasing the diffusivity in the thin implant zone, leaving the diffusivity in the rest of the sample as defined by Frauenfelder [5]. At the lower temperatures, a diffusivity of 5.0×10^{-6} cm^2/s was defined for this thin layer. This diffusivity was not imposed on the higher temperature experiments where the Frauenfelder values exceeded this migration rate. The retention results are shown in Fig. 1. The modification corrects the simulation at the lower temperatures. The diffusivity may not actually increase in reality, but this modification simply indicates the need for a mechanism that releases the hydrogen from the surface at a higher rate than expected.

3.2. Retention vs. flux

Fig. 2 shows the retention measurements for samples WW-15, WW-16, and WW-17. The retention values are given in total hydrogen isotope atoms (D + T) per square centimeter. In these experiments, the exposure temperature was kept constant at 623 K, and the flux was varied as shown in Table 1. The results of the model when applied to the retention vs. temperature experiments are also shown in Fig. 2 along with the experimental data. The model predicts the retention values quite well. The agreement between the TMAP modeling and the experimental data gives credibility to the estimated data point added to Fig. 1.

3.3. Surface mechanisms

3.3.1. Scanning electron microscopy

Several ÆSAR foil samples and one Plansee sample were exposed to deuterium-only plasmas and analyzed by Scanning Electron Microscopy. The exposure conditions are shown in Table 1. Sample F-12 was not annealed prior to exposure, and the SEM micrograph (Fig. 3(a)) shows blisters of 1–10 μm in diameter, many of which have ruptured. No change in the surface was observed in sample F-17, which was annealed to 1273 K (not shown in the figure). However, the SEM of sample F-18, which was annealed to 1473 K (Fig. 3(b)), shows a sparse population of small bubble approximately 1–3 μm in diameter. Sample W-19 (again, not shown in the figure) was a powder-metallurgy product from Plansee for which no blisters were observed after a 1273 K anneal and a 1.2×10^{21} ions/cm^2 exposure at 373 K.

3.3.2. Discussion

It is not clear at what fluence or temperature the bubbles grow to sufficient size to form observable blisters on the surface. Sze et al.[7] reported blisters of tens of microns on a high purity, unannealed, tungsten foil sample at fluences of 10^{22} D/cm^2 at 400 K, while no blisters were observed on samples exposed at 1250 K. Haasz et al. [8] reported blisters 10–50 μm in diameter

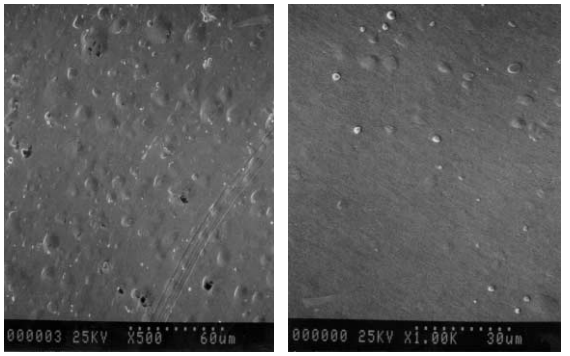

Fig. 3. SEM micrographs of sample F-12 (a) not annealed; and F-18 (b) annealed to 1473 K. Exposure conditions in both (a) and (b) were 1.7×10^{18} ions/cm^2 s for 30 min at 423 K.

on tungsten samples exposed to 500 eV deuterium ions to a fluence of $>10^{20}$ D^+/cm^2 at 500 K. The samples were annealed to >1473 K for one hour prior to implantation. In the present work, no blisters were observed in samples annealed at 1273 K. van Veen et al. [9] examined the effects of annealing on vacancies in tungsten created by high energy proton and electron beams. Vacancies were seen to coalesce into voids containing 11–16 vacancies after annealing at 1200 K. Higher annealing temperatures created voids containing 40–60 vacancies. It is possible that higher annealing temperatures serve to create larger clusters of vacancies. Voids existing in sample F-18 may have been larger than those in F-17 and W-19, causing sample F-18 to blister earlier.

In the retention experiments, the samples were annealed to 1273 K. No samples annealed at this temperature showed blister formation, or any other change in the surface, even at the highest magnification. Only speculation can be made concerning the mechanism that would enhance the emission at lower temperatures. It is possible that the bubbles on sample F-17 and W-19 were very small. The enhanced re-emission of hydrogen at lower temperatures may be explained by a dynamic mechanism of nano-scale bubble formation and the creation of short-circuit paths to the surface. At higher temperatures, the diffusion into the material will be faster; fewer bubbles will form near the surface. Traps will still be active, and bubbles will form deeper in the material, so retention will be high. At even higher temperatures, the traps will not be active, and the solubility will be sufficient to keep most of the hydrogen in solution. Hydrogen can quickly diffuse through the material and escape, lowering the retention.

4. Conclusion

Samples of 99.95% pure tungsten were exposed to high fluxes of 100 eV deuterons and tritons. Total retention values are low at low and high temperatures, with a peak at approximately 623 K. TMAP4 simulations were capable of reproducing the high temperature results, but the model failed at low temperatures. A thin implant zone with an enhanced diffusivity was added to the model at lower temperatures to increase the hydrogen release rate. This modification was sufficient to reproduce the lower temperature data. SEM analysis of samples exposed to D^+ at low temperatures revealed, in some cases, the formation of blisters on the surface. It is speculated that, at low temperatures, the slow diffusion of hydrogen leads to a near-surface concentration sufficient to form bubbles that nucleate at existing voids. This leads to blister rupture or microcrack formation creating short-circuits to the surface. Although an enhanced release is beneficial in terms of tritium retention, sudden blister cracking and surface exfoliation may lead to tungsten material being injected into the plasma – a highly unfavorable scenario for plasma fusion machines.

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