Deuterium retention and thermomechanical properties in ion-beam displacement-damaged tungsten

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Abstract: Retention of plasma-implanted D is studied in W targets damaged by a Cu ion beam at up to 0.2 dpa with sample temperatures between 300 K and 1200 K. At a D plasma ion fluence of 10^{24}/m^2 on samples damaged to 0.2 dpa at 300 K, the retained D retention inventory is 4.6x10^{20} D/m^2, about \sim 5.5 times higher than in undamaged samples. The retained inventory drops to 9x10^{19} D/m^2 for samples damaged to 0.2 dpa at 1000 deg K, consistent with onset of vacancy annealing; at a damage temperature of 1200K retention is nearly equal to values seen in undamaged materials. Nano-scale thermal diffusivity techniques are also used to provide thermo-mechanical data from the near-surface damaged region. Thermal conductivity of W damaged to 0.2 dpa at room temperature drops from the un-irradiated value of 182\pm3.3 W/m-K to 53\pm8 W/m K. The results have significant implications for the performance of W-based plasma-facing components, tritium inventory management and fuel self-sufficiency in fusion energy systems.

1.0 Introduction

Fusion engineering test reactor concepts that demonstrate steady-state reactor-relevant operations with a closed tritium fuel cycle and begin to produce useful energy are expected to have material surfaces that must withstand intense heat fluxes reaching 10 MW/m\(^2\) or more at the divertor target with particle fluxes of 10^{19} - 10^{20} /m^2-sec at the first wall and 10^{23} - 10^{24} /m^2-sec at the divertor. With expected operational duty cycles the displacement damage from energetic neutron irradiation is anticipated be a few dpa/year which is expected to produce alloying by transmutants at a level of about 1 at. %/year and volumetric He production of \sim 5 appm/year in the wall and divertor armor materials.

Based on these considerations, tungsten-based alloys (W) have been proposed as a possible solid material for use in the first wall and divertor target regions [1, 2]. If the W thermal conductivity were to suffer degradation e.g. due to irradiation effects with a fixed target heat flux, it is likely that with existing divertor designs[3, 4] near-surface recrystallization would occur, increasing the risk of brittle fracture and armor failure. Thus thermo-mechanical materials property evolution under the combined action of plasma and displacement damage irradiation is important for credible divertor designs. Furthermore, the retention of T in the first wall and divertor is a well recognized additional challenge for both tritium inventory control and achieving a closed tritium fuel cycle[5, 6]. For a tritium breeding ratio TBR>1 and effective wall recycling coefficient R<1, a straightforward particle balance [7] shows that the probability of permanently trapping tritium in the material surfaces of the devices, \(p_{\text{trap}}\), must satisfy

\[ p_{\text{trap}} < (TBR - 1)(1 - R) \frac{p_{\text{burn}} \eta_{\text{fuel}}}{1 - p_{\text{burn}} \eta_{\text{fuel}}} \]
where $p_{\text{burn}} < 1$ is the tritium burn-up probability and $\eta_{\text{fuel}} < 1$ is the efficiency of fueling the core plasma region by injecting fuel across the plasma boundary. With typical values $\text{TBR} \approx 1.05$, $R \approx 0.99-0.999$, $p_{\text{burn}} \approx 0.05$, and $\eta_{\text{fuel}} \approx 0.2-0.3$, we then estimate an upper limit of $p_{\text{nap}} < 10^{-6} - 10^{-7}$. Thus fusion fuel retention in radiation damaged W operating under relevant conditions is also of interest. Motivated by these considerations, we present experiments focused on retention and thermo-mechanical property evolution in ion-beam damaged W materials.

2.0 Previous Work

Hydrogen isotope retention physics mechanisms in plasma-exposed tungsten have been extensively studied. Hydrogen isotopes are mobile in tungsten at the expected temperatures in fusion experiments[8]. Thus deuterium atoms implanted by the plasma in the near surface (few nm’s) region can diffuse into the bulk region, forming a spatially decaying profile deeper into the material. As they diffuse, deuterium atoms can become trapped at grain boundary, dislocation, and vacancy defect sites as well as at precipitate (i.e. void, bubble or blister) sites. The trapping energy (i.e. the energy which a trapped particle must acquire to escape the trap) can vary considerably depending on both the type of trap as well as on the number of atoms already contained within the trap; theoretical calculations suggest that it can vary from ~0.2-0.3eV up to 1.5eV or more[9-11] depending on the trap type.

A number of earlier papers have reported experimental studies of this problem; with a few notable exceptions most of this work has used energetic ion beams as a surrogate for the neutrons. Increased retention of plasma-implanted D was reported in light (D, He) ion-beam damaged single crystal [12] and polycrystalline [13] W. The results showed evidence of higher energy traps presumably from displacement damage-induced vacancies. The increased retention that was observed at lower temperature was largely/wholly eliminated when damaged material was subsequently annealed at ~1200 K. However this earlier work does not address the key question of whether the annealing rate is sufficiently high as compared to the anticipated damage rate, and thus does not address whether or not annealing can be expected in neutron-generating fusion systems. The retention increase appeared to saturate when the damage level approached 0.4 dpa or so [14]. Retention of D in self-damaged W (i.e. in W exposed to a W ion beam) due to subsequent high-flux D plasma exposures has been reported [15]. A marked increase in retention was reported for 300-500K plasma exposures, and the increase was found to saturate as the damage level approached 0.6 dpa or so. A much smaller increase in retention was found for sample temperatures of 700-1000 K. Similar results were reported in [16]; in this work in-situ TEM imaging also showed that smaller sizes defects merged into one another at elevated temperatures, forming a lower density of larger vacancy clusters. Similar results were reported when the plasma ion flux approaches values expected in divertor target of engineering test reactors[17]. Finally, the presence of damage also affected the observed D profile evolution[18], particularly with higher implanted D ion fluences.

Shimada and collaborators have carried out plasma-implanted D retention studies in neutron-damaged W [19-24]. NRA was used to find the near-surface retained D and was compared to TDS. TDS shows significantly more retained D than does NRA, providing indirect evidence for deep (>10 micron) D retention in n-damaged W. In addition, D retention began to saturate at higher plasma fluence in a manner reminiscent of ion-beam damage results. These
workers also reported a different, broader range of release temperatures of D during TDS, suggesting that the trap energy distribution is different in the two types of damage studies. Initial studies of thermal conductivity in displacement-damaged plasma facing tungsten armour [25] report significant (~factor of 2 or more) reduction in thermal diffusivity (and thus in thermal conductivity) for 0.2 dpa tungsten damaged by a He ion beam. The results were compared favorably with published models of defect scattering of electrons, the main heat carriers in W.

3.0 Experimental Techniques

For the experiments reported here, W samples were prepared as documented elsewhere [26], and were then damaged at the Ion Beam Materials Laboratory (IBML) at LANL. A Cu ion beam with energy between 0.5-5.0 MeV was used to induce uniform displacement damage in the first ~1 µm of a W surface that was held at a controlled temperature ranging from 300-1200 K during ion beam exposure. The specific damage level corresponding to the ion beam fluence on the surface was determined from SRIM (Stopping and Range of Ions in Matter) Monte Carlo code calculations as described elsewhere [26]. Samples were then held at a temperature of 380K and exposed to a D plasma in a helicon RF-produced plasma device [27] (in these experiments the source was operated as an unmagnetized inductively coupled source). A 100eV ion current density of 4x10^20 ions/m^2-sec with an exposure of 10^4 seconds provided a fluence of 10^{24} ions/m^2. NRA profiles of trapped D were obtained using a 3He^+ ion beam with energies of 0.6, 0.8, 1.2, 1.6, 2.0, 2.5, and 3.5 MeV to obtain the optimum depth resolution at different depths. The results then provide D profiles with resolution of less than 1 µm up to a depth of ~6 µm in W. Thermal desorption spectroscopy (TDS) was used to measure D release temperatures and total D inventory. A detailed discussion of these techniques is available[7][26]. The thermal conductivity was studied using the 3ω technique that we have described elsewhere [28]. Briefly, a thin insulation layer of 30 nm thick Al2O3 was deposited via atomic layer deposition (ALD) at 250 °C on the sample surface. A metal strip, made of 25 nm thick Cr and 125 nm thick Au, was deposited and patterned on top of the insulation layer. The metal strip works both as a heater and a thermometer. By applying higher frequencies to shorten the thermal penetration depth, this frequency domain technique can probe thermal properties within the near-surface damage region.

4.0 Experimental Results

FIG. 1 shows D retention results from TDS for samples damaged under conditions where the sample temperature was controlled during the ion beam exposure. For low temperature damage exposures, the results show a clear increase in retention, associated presumably with higher energy traps, as shown by the elevated TDS D release rate when the sample temperature during TDS reaches 700-1000K. The relative increase of retention over that found in an undamaged sample obtained from both TDS and NRA measurements [26] shows retention proportional to dpa^{-0.66}. The temperature of the sample during the displacement damage process play an important role in the total retention, as can be seen in FIG. 1. For a sample damaged at 300 K (blue curve, FIG. 1) we observe two broad release features, one between 400-600 K, and a second release feature between 700-1000K that contains most of the retained inventory with a peak release rate occurring during TDS at a temperature of about 820 K. Samples that were damaged at 1240 K show a retained D release profile that is nearly identical to the control TDS release profile, obtained for W samples that were implanted with the same plasma D ion fluence but which were not subject to any displacement damage. This result provides a key new result: in particular, even with the
elevated damage rates of these ion beam experiments, the annealing process occurs at a high enough rate to largely eliminate increased retention, provided that the damaging is occurring at a sufficiently high temperature. It then follows that similar annealing should then be expected at the lower damage rates ($10^3$-$10^4$ times slower than these ion beam experiments) that are expected to occur due to neutron damage in burning plasma experiments.

FIG. 1: TDS D release rate for undamaged W sample (black line), and for W samples damaged to 0.2 dpa with the temperature during damage as the controlled variable. Damaged samples were implanted with 100eV D plasma ions $10^{24}$ ions/m$^2$ fluence. Retention is strongly reduced as sample damaging temperature is increased, indicating annealing rate is high enough to overcome the high ion beam damage rate; the results imply that neutron damage in PFCs can be annealed by operating the wall at sufficiently high temperature.

Measurements of the thermal conductivity of the damaged layer were also performed for Cu-ion beam damaged W samples. Here the damage profile was held uniform up to a depth of 1 micron by using multiple ion beam energies to induce the desired dpa profile. Results (FIG. 2) show that samples damaged at room temperature exhibit a measurable decrease in thermal conductivity even at $10^2$ dpa. The decrease appears to begin to saturate at a value of roughly 50 W/m-K as the damage level begins to exceed 0.1 dpa, a factor of ~3x lower than the undamaged value. Similar reductions in thermal conductivity are found for damaging temperatures ranging from 20 deg C up to 500 deg C.

5.0 Discussion

The retention results reported here are consistent with a number of previously reported findings. In particular, in samples damaged at low temperature, we have observed a clear increase in retention with increasing damage. This increased retention occurs in the region where displacement damage is computed to occur, and is associated with traps that release the D atoms at high (~850 K) temperature.

Furthermore, the rate of retention increase with increased damage begins to saturate at elevated levels of damage. We also find a clear decrease in the retention in these deeper traps when damage occurs at sufficiently high (~1000-1200 K) temperatures. Unlike earlier work where damaging was imposed at low temperature, and then a subsequent annealing cycle was applied, the results here were obtained with the sample being held
at a controlled high temperature during the damaging process. As a result, our experimental results show that the annealing rate can be sufficiently high to overcome the rate of displacement damage and subsequent formation of vacancies. Because neutron damage rates are much lower than the ion beam damage rates, it then follows that annealing in burning plasma experiments should be capable of removing much of the damage that will occur in that environment. These retention effects are observed at damage levels (~0.1 dpa) that would correspond to only a few weeks of operation under projected DEMO device operations[29] and are large enough to impact tritium breeding and inventory control.

The reduction in thermal conductivity reported here is quite significant and, should it occur in a burning plasma experiment due to neutron damage, would then have very significant implications for the performance of high heat flux components such as the divertor target region. Furthermore, our results are in reasonable agreement with recent results obtained in 0.2 dpa He-ion beam damaged W using a different non-contact technique to measure thermal diffusivity[25]. However, we note that the one published study of thermal conductivity in neutron-damaged W show only much more modest (~20-30%) reductions in thermal conductivity[30]. As discussed earlier, the performance of the divertor target is extremely sensitive to this parameter; thus it is essential to study this in more detail to determine how seriously radiation damage-induced thermal conductivity degradation will impact divertor design.

The earlier discussion of TBR motivates us to estimate the trapping probability, \( p_{\text{trap}} \), introduced earlier in this paper for plasma exposed W. Recent work[31] provides measurements of retained inventory vs plasma fluence for undamaged tungsten. Taking \( p_{\text{trap}} \) to be given by the ratio of these two measurements, we can then examine the evolution of \( p_{\text{trap}} \) vs. plasma ion fluence. These results (FIG. 3) show a precipitous drop in \( p_{\text{trap}} \) with increased plasma fluence, presumably due to the fact that as the fluence is raised, the near-surface intrinsic traps become filled with D. The resulting saturated near-surface region is then more likely to release D back to the plasma, thereby reducing \( p_{\text{trap}} \). If the plasma has a mixture of He ions incident on the W surface,
a thin (20-30 nanometer) layer of He-filled nanobubbles can form when the surface temperature is below a critical value. This nanobubble layer has been found to act as a strong diffusion barrier for plasma implanted D ions[32] and, as a result, the trapping probability drops further, as shown in FIG. 3. Modeling these undamaged experiments and the effect of elevated temperature on retention, we anticipate that the retention probability in undamaged W at 1000 K would be well below the threshold required for TBR>1.

FIG. 3: Retained fraction of deuterium in tungsten versus total plasma fluence. The retained fraction decreases as the total plasma fluence is increased, due to the gradual saturation of trap sites within the material. Existing experimental data in tungsten damaged to 0.2 dpa shown. Vertical colored areas show the expected fluence to a DEMO first wall (FW) for several operational periods. Undamaged data points derived from published results[31]. Neutron data from Shimada et al[22].

We can also use the results of these ion beam experiments to examine the behavior of retention probability in damaged W material. The results presented in this paper were obtained at a low plasma ion fluence of $10^{24}$ ions/m$^2$. When recast as a retention probability, the results from 0.2 dpa damaged W at room temperature shows a very high ($\sim5\times10^{-4}$) retention probability; when the damage occurs at high temperature (1000-1200 K) this value falls back to a value of $1\times10^{-4}$, close to the undamaged value. These two values are shown as the blue circles in FIG. 3. Published retention data from neutron irradiation[22] is also shown in FIG. 3 as well. These damaged W retention data points show a trend of decreasing $p_{\text{trap}}$ with increased fluence, and it appears that the slope of this trend is comparable to that found for undamaged W. These trends suggest that the value of $p_{\text{trap}}$ in W damaged to levels of 0.2-0.3 dpa would be small enough to allow TBR>1 once the fluence exceeds $\sim10^{26}$ ions/m$^2$-sec. This plasma fluence to the first wall would occur in about one week of operation in DEMO. However, we point out that further experiments in damaged W at higher fluence (and thus with deeper damage profiles to account for deeper D diffusion) are necessary to demonstrate that this is indeed the case.

6.0 Conclusions

We have observed a clear increase in D retention in room temperature damaged tungsten up to levels approaching $\sim0.2$ dpa. This increased retention occurs in the
region where displacement damage is computed to occur, and is associated with traps that release the D atoms at high (~850 K) temperature. We also find a clear decrease in the retention in these deeper traps when damage occurs at sufficiently high (~1000-1200 K) temperatures. These retention effects are observed at damage levels (~0.1dpa) that would correspond to only a few weeks of operation under projected DEMO device operations and are large enough to be of significance for tritium breeding and inventory control. We also observe a pronounced reduction in thermal conductivity in displacement damaged W that, should it occur in neutron damaged material, would have significant implications for the performance of a divertor target.

Acknowledgement: This work supported by grants from the U.S. Department of Energy Office of Science DE-FG02-07ER54912 and from the University of California Office of the President 12-LR237801. Los Alamos National Laboratory is an affirmative action equal opportunity employer, and is operated by Los Alamos National Security, LLC, for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396. Mas.

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