High flux irradiations of Li coatings on polycrystalline W and ATJ graphite with D, He, and He-seeded D plasmas at Magnum PSI

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Lithium wall conditioning on PFCs (Plasma Facing Components) on a variety of substrate platforms (e.g. graphite, Mo, etc...) has resulted in improved plasma performance on multiple magnetic fusion devices. On graphite, this improvement occurs through the control of retention and recycling of hydrogen at the plasma-material interface by the chemical bonding of Li, O, and D at the surface. Moderate fluence ($1 \times 10^{21} \text{ m}^{-2}$) studies of Li on W, performed in PRIHSM (Particle Radiation in Hard and Soft Matter), demonstrated that H retention is similar to Li on ATJ graphite but He ions, when mixed in a D beam, can inhibit the retention. To expand these studies closer to reactor relevant regimes like inside ITER, irradiations were carried out in Magnum-PSI at DIFFER up to fluences of $\sim 10^{25} \text{ m}^{-2}$ with D, He, and He-seeded D plasmas (He 5-10%). Results show that D is still retained at higher fluxes and fluences.

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1. Introduction

One of the next significant steps for the advancement of fusion energy is a PFC that can withstand the extreme environments of a burning plasma fusion device such as ITER. Materials with high melting temperatures such as graphite and tungsten (W) have been selected due to their attractive thermo-mechanical properties under high heat loads. However, graphite will chemically erode with hydrogen isotopes [1] and the well known co-deposition issues with tritium has rendered this material incompatible for environments expected in the ITER divertor region. Furthermore, recent work has shown serious issues for coarse-grained W materials. Tungsten will undergo microstructure changes (i.e. blisters, bubbles, holes, and/or fuzz) under low energy D and He ion irradiation conditions below the damage threshold, limiting its beneficial properties [2–4]. Furthermore, recent work that studies both steady-state and transient events (e.g. ELM-like events) on tungsten have demonstrated key challenges to the use of tungsten even at moderate heat load levels ($\sim 0.2 \text{ GWm}^{-2}$) resulting in surface morphologies that may compromise the performance of the W PFC [I3 PSI 2014; O6 PSI 2014].

A potential method to counteract this damage is through the use of low-Z coatings such as lithium. Recent work by Baldwin demonstrated that small amounts of low-Z metallic impurities in the plasma (i.e. 0.1% of Be and C) can also affect the formation of the surface microstructures induced by D/He exposures. These studies demonstrated that metallic impurities seeded in high-flux plasmas can create a protective coating on the surface of the W such as a W-C layer or a W-Be alloyed layer [5]. These coatings appear to prevent the formation of fuzz, which also results in lower melting points for the new alloy. In the case of lithium multiple machines have seen significant improvement in plasma performance with Li coatings on PFCs

[6]. This improvement is the result of lithium's ability to pump D, reducing D recycling [7] and ELM instabilities. Investigations involving coupled atomistic computational simulations and *in-situ* irradiation using lithiated graphite indicate that Li alone does not retain D. In fact, the Li getters O to the surface, which then binds with the hydrogen isotopes [8].

In the context of synergistic conditions with He and D plasmas, studies with simultaneous and sequential He and D ion beams and He-seeded D plasmas have demonstrated changes to hydrogen retention behavior. Lee *et al.* performed studies of D retention in W under both sequential and simultaneous beams of D and He ions and found that the He ions will create additional damage sites that became trapping sites for D[9]. In a later study testing H permeation in thin samples, they observed that the He, during simultaneous irradiations, created a diffusion barrier to H that lessened its permeation through the W[10]. Using He seeded plasmas, other studies have seen a reduction of D retention into the bulk of W because of the He [5,11,12]. This work presents results on the effect Li coatings on commercial-grade W and ATJ graphite can have on the retention behavior of D under high flux plasmas ($<10^{21} \text{ cm}^{-2}\text{s}^{-1}$) in Magnum PSI at DIFFER.

2. Experimental

The samples used for these experiments were three W (99.9% pure) discs and one ATJ graphite square. The W discs were 10 mm in diameter and 3 mm in thickness. The ATJ graphite samples were roughly 10 mm on a side and ~3 mm thick. Both types of samples were mechanically polished to mirror-like surfaces.

Lithium was deposited onto the samples using a device similar to the LITER device used on NSTX [13]. The coating thickness was determined using a deposition rate measured from a quartz crystal microbalance (QCM). This deposition rate was 2–

4 Å/s, with a final thickness for Li thin-films of either 100 or 500 nm for the W substrates samples and 1.0-µm Li films on the graphite substrate samples.

Plasma exposures were carried out in Magnum PSI. The first sample (CW-Li2HF) was exposed to a He seeded D plasma up to a fluence of $\sim 5 \times 10^{24} \text{ m}^{-2}$ at a surface temperature between 200 and 300°C, where the He gas flow rate was 33.3% of the total flow. Flow rate is listed here because there is no direct way to measure the ion fraction. The second and third samples (CW-Li3HF and CW-Li5HF) were exposed to a He plasma up to a fluence of $\sim 5 \times 10^{24} \text{ m}^{-2}$ and a D plasma up to a fluence of $\sim 5 \times 10^{25} \text{ m}^{-2}$ respectively. The surface temperature of CW-Li3HF was comparable to CW-Li2HF but CW-Li5HF. However due to cooling problems initially for the first 20% of the exposure sample CW-Li3HF was heated up to between 400 and 500°C, and then was brought down to the temperature of the other two samples (e.g. $\sim 200\text{-}300^\circ\text{C}$). All of the W samples were biased to -30 V. The ATJ graphite sample was exposed to D plasma up to a fluence of $3 \times 10^{24} \text{ m}^{-2}$.

To perform surface analysis, SEM, XPS, and SIMS were used to measure the surface morphology and the surface chemistry respectively. Both procedures were carried out in the Frederick Seitz Materials Research Laboratory Central Research Facilities, University of Illinois. The SEM was a Hitachi S-4700 High Resolution microscope and the XPS system was a Physical Electronics PHI 5400 using a magnesium filament. Due to exposure to atmosphere during sample transfer from vacuum and during transport, a passivated layer forms because of lithium's high chemical reactivity [14]. This layer is removed in the XPS measurements above by sputtering with 1 keV Ar ions for 15-20 minutes to expose the chemistry induced in the film from the plasma exposure. This approach was developed by Taylor et.al. [14] and the method adjusted in this work for a thinner film. Additionally, SIMS was

utilized to confirm the composition on the surface. Depth profiles were performed on a Cameca ims 5f dynamic SIMS using O₂ ions at 100 nA to perform the analysis with a raster of 250 μ m.

3. Results and Discussion

The SEM measurements of the W samples with a 100 nm Li coating show a unique surface morphology change after irradiation with a He-seeded D plasma. As observed in figure 1, the surface has numerous cracks in the surface where it was exposed to the plasma. This cracking could be the result of the coating changing rapidly from a liquid, which results from beam heating on the surface, to a solid after exposure. This needs to be investigated further, however given the temperature increase above 200 °C (i.e. melting point of Li is 180 °C) due to the high-heat flux plasma a change in phase for the Li constituent is plausible. When a micrograph was taken with back-scattered electrons (BSE), in figure 2b, there is a change in the atomic number within the cracks, which are marked by black circles. Because of the lighter shade marked by the circles in figure 2b, the film appears to be Li. The low contrast between the two regions of atomic number could be the result of shadowing from the coating given the small areas of high Z. XPS measurements of the same sample, after cleaning, do not show a peak within the Li 1s region scan (figure 3a). This is not unexpected because of an energy loss peak that appears in the XPS spectrum for W around 56 eV that could be covering the Li 1s peak at ~54 eV. Tungsten is clearly visible on the surface from the W 4f spectra in figure 3c. For further clarification each sample was measured using SIMS (figure 4) looking for H, Li, and W. The line for Li in the profile of CW-Li₂HF (figure 4a) indicates a persistent layer of Li on the surface due to the steady state profile obtained. In contrast, the profiles for CW-Li₃HF and CW-Li₅HF, in figure 4b and 4c respectively,

show Li having a higher count initially and then reducing after time. The reason for the difference in the Li traces is unclear and will be studied further. However, all three traces confirm the presence of Li on the surface. More importantly, the results also points to what appears to be a self-healing mechanism at the surface. Calculating the expected Li thin-film erosion from He/D bombardment at 30 eV (i.e. sputter yield = 0.05 atoms/ion) and a fluence of $5 \times 10^{20} \text{ cm}^{-2}$ the expected eroded thickness of Li is about 5.3 μm and with the measured thickness before exposure to plasma of 100-nm this results in a factor of about 50 increase in lifetime of the Li layer. For sample CW-Li2HF this could have been higher given the persistent Li layer evidenced by SIMS. Similarly, for the other two samples lifetime increase by at least a factor between 50-100 is achieved. This is a lower bound estimate however since the exposure was stopped at fluences between 10^{20} - 10^{21} cm^{-2} .

Observing the O1s spectra, there is a peak at $\sim 530 \text{ eV}$. This peak indicates a Li-O bond existing on the surface. In figure 3c, there is a peak around 533 eV, which is associated with the Li-D-O complex [15]. The lack of this peak in the He only and He seeded plasma indicates no Li-D-O bonding was able to form, confirming earlier observations of He-induced break-up of D-O bonds for the Li-D-O phase. For the seeded plasma, this is likely the result of He ions preventing or eliminating that complex, especially given the 2 to 3 order of magnitude increase in fluence from previous ion beam studies. The missing peak around 533 eV, after cleaning, for the D only case is unexpected given that NSTX ATJ samples have maintained that Li-D-O chemistry well after exposure, likely due to carbon's high permeability [14].

The other O 1s spectra, presented in figure 5a, for the ATJ graphite exposed to high flux deuterium plasmas show a peak with a binding energy at $\sim 533.3 \pm 0.6 \text{ eV}$. This peak persists throughout the cleaning process, which implies that the D retention

mechanism is maintained up to high fluxes and fluences. In support of the O 1s spectra, the Li 1s peak splits upon cleaning as seen in figure 5c. That split is characteristic of the behavior of the energy region for low-flux experiments [16]. In addition, the C 1s spectra also support the prolonged D retention with the peak that occurs around 292 eV (figure 5b) [15]. This result elucidates earlier results with lower flux (ion-beam based) studies that tended toward a saturation point of $\sim 10^{21} \text{ m}^{-2}$ as fluence increases, which is 1000 times lower than this case [17]. We suspect that this behavior is due to super-saturation of D implantation near the surface-dominated lithiated graphite structure likely competing with mechanisms of both high-flux induced erosion and ion-induced mixing of implanted D with lithium and oxygen atoms. The primary mechanism of large-flux and large fluence irradiation on lithiated graphite and the role of oxygen on D retention is the subject of future studies.

4. Conclusions

Lithium coatings on tungsten and ATJ graphite were exposed D, He, and mixed D and He plasmas. These samples were characterized using SEM and XPS. The SEM results show a cracked surfaced coating. A BSE micrograph shows a lower Z coating over the tungsten substrate. XPS spectra of the samples show the Li-O complex but do not show a peak in the Li 1s region scan, though this is likely the result of a W energy loss peak, however the presence of Li was confirmed using SIMS. The graphite samples showed the retention behavior typically found in controlled experiments in the XPS spectra. With the prominent peak at $533.3 \pm 0.6 \text{ eV}$, the retention persists into high flux and fluence conditions. This expands the saturation predicted at lower fluences that has been observed previously. Further experiments, searching for a high flux saturation point, will help to predict the D pumping endurance of lithiated graphite in tokamaks.

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References

- [1] P.C. Stangeby, O. Auciello, A.A. Haasz, J. Vac. Sci. Technol. Vac. Surf. Films 1 (1983) 1425.
- [2] W. Wang, J. Roth, S. Lindig, C.. Wu, J. Nucl. Mater. 299 (2001) 124.
- [3] D. Nishijima, M.. Ye, N. Ohno, S. Takamura, J. Nucl. Mater. 329-333, Part B (2004) 1029.
- [4] M.J. Baldwin, R.P. Doerner, J. Nucl. Mater. 404 (2010) 165.
- [5] M.J. Baldwin, R.P. Doerner, D. Nishijima, K. Tokunaga, Y. Ueda, J. Nucl. Mater. 390–391 (2009) 886.
- [6] M. Ono, M.G. Bell, Y. Hirooka, R. Kaita, H.W. Kugel, G. Mazzitelli, J.E. Menard, S.V. Mirnov, M. Shimada, C.H. Skinner, F.L. Tabares, Nucl. Fusion 52 (2012) 037001.
- [7] M.G. Bell, H.W. Kugel, R. Kaita, L.E. Zakharov, H. Schneider, B.P. LeBlanc, D. Mansfield, R.E. Bell, R. Maingi, S. Ding, S.M. Kaye, S.F. Paul, S.P. Gerhardt, J.M. Canik, J.C. Hosea, G. Taylor, the NSTX Research Team, Plasma Phys. Control. Fusion 51 (2009) 124054.
- [8] P.S. Krstic, J.P. Allain, C.N. Taylor, J. Dadras, S. Maeda, K. Morokuma, J. Jakowski, A. Allouche, C.H. Skinner, Phys. Rev. Lett. 110 (2013) 105001.
- [9] H.T. Lee, A.A. Haasz, J.W. Davis, R.G. Macaulay-Newcombe, D.G. Whyte, G.M. Wright, J. Nucl. Mater. 363–365 (2007) 898.
- [10] H.T. Lee, H. Tanaka, Y. Ohtsuka, Y. Ueda, J. Nucl. Mater. 415 (2011) S696.
- [11] O.V. Ogorodnikova, T. Schwarz-Selinger, K. Sugiyama, V.K. Alimov, J. Appl. Phys. 109 (2011) 013309.
- [12] M. Miyamoto, D. Nishijima, M.J. Baldwin, R.P. Doerner, Y. Ueda, K. Yasunaga, N. Yoshida, K. Ono, J. Nucl. Mater. 415 (2011) S657.
- [13] H.W. Kugel, D. Mansfield, R. Maingi, M.G. Bell, R.E. Bell, J.P. Allain, D. Gates, S. Gerhardt, R. Kaita, J. Kallman, S. Kaye, B. LeBlanc, R. Majeski, J. Menard, D. Mueller, M. Ono, S. Paul, R. Raman, A.L. Roquemore, P.W. Ross, S. Sabbagh, H. Schneider, C.H. Skinner, V. Soukhanovskii, T. Stevenson, J. Timberlake, W.R. Wampler, J. Wilgren, L. Zakharov, J. Nucl. Mater. 390–391 (2009) 1000.
- [14] C.N. Taylor, K.E. Luitjohan, B. Heim, L. Kollar, J.P. Allain, C.H. Skinner, H.W. Kugel, R. Kaita, A.L. Roquemore, R. Maingi, Fusion Eng. Des. 88 (2013) 3157.
- [15] C.N. Taylor, B. Heim, J.P. Allain, J. Appl. Phys. 109 (2011) 053306.
- [16] C.N. Taylor, J.P. Allain, K.E. Luitjohan, P.S. Krstic, J. Dadras, C.H. Skinner, Phys. Plasmas 1994-Present 21 (2014) 057101.
- [17] C.N. Taylor, J.P. Allain, B. Heim, P.S. Krstic, C.H. Skinner, H.W. Kugel, J. Nucl. Mater. 415 (2011) S777.

Figure Captions

Figure 1: SEM micrographs showing cracking on the surface of the W samples after mixed D and He plasma irradiation. It appears to be a cracked thin film. Image b) is a close-up of the space in between the cracks.

Figure 2: SEM micrographs, secondary electron (a) and backscattered electron (b), showing a change in atomic number within the irradiation zone.

Figure 3: XPS region scans of O 1s, Li 1s, and W 4f after high flux D irradiation of Li on W. These plots show before and after cleaning for a) CW-Li₂HF, b) CW-Li₃HF, and c) CW-Li₅HF. Scan a) corresponds to the SEM micrographs above. These other scans show no indication of Li on the surface in the Li 1s region but potentially a Li-O peak in the O 1s region.

Figure 4: Plot of SIMS depth profiles for the samples exposed to (a) D/He, (b) He, and (c) D. The traces indicate the presence of Li on the surface of the samples even after they were cleaned for the XPS analysis. The jog in Li trace is a result of switch between ion detectors and the dashed line accounts for that switch.

Figure 5: XPS region scans of O 1s, C 1s, and Li 1s after high flux D irradiation. The upper plots show before and after cleaning. They show that the Li-D-O functionality near 533 eV continues up to high fluence irradiation. This is consistent with experiments performed previously, which are the lower plots. [15]

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5