High-flux plasma exposure of ultra-fine grain tungsten

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In this work, we examine the response of an ultra-fine grained (UFG) tungsten material to high-flux deuterium plasma exposure. UFG tungsten has received considerable interest as a possible plasma-facing material in magnetic confinement fusion devices, in large part because of its improved resistance to neutron damage. However, optimization of the material in this manner may lead to trade-offs in other properties. We address two aspects of the problem in this work: (a) how high-flux plasmas modify the structure of the exposed surface, and (b) how hydrogen isotopes become trapped within the material. The specific UFG tungsten considered here contains 100 nm-width Ti dispersoids (1% wt.) that limit the growth of the W grains to a median size of 960 nm. Metal impurities (Fe, Cr) as well as O were identified within the dispersoids; these species were absent from the W matrix. To simulate relevant particle bombardment conditions, we exposed specimens of the W-Ti material to low energy (100 eV), high-flux ($> 10^{22} \text{ m}^{-2} \text{ s}^{-1}$) deuterium plasmas in the PISCES-A facility at the University of California, San Diego. To explore different temperature-dependent trapping mechanisms, we considered a range of exposure temperatures between 200 °C – 500 °C. For comparison, we also exposed reference specimens of conventional powder metallurgy warm-rolled and ITER-grade tungsten at 300 °C. Post-mortem focused ion beam profiling and atomic force microscopy of the UFG tungsten revealed no evidence of near-surface bubbles containing high pressure D₂ gas, a common surface degradation mechanism associated with plasma exposure. Thermal desorption spectrometry indicated moderately higher trapping of D in the material compared with the reference specimens, though still within the spread of values for different tungsten grades found in the literature database. For the criteria considered here, these results do not indicate any significant obstacles to the potential use of UFG tungsten as a plasma-facing material, although further experimental work is needed to assess material response to transient events and high plasma fluence.

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I. INTRODUCTION

Understanding the interaction between the plasmas created in magnetic-confinement fusion devices and the materials that comprise the interior surfaces presents arguably one of the most challenging problems in materials science. A unique issue is the complexity and extraordinary harshness of the fusion environment: the materials must be able to accommodate particle bombardment conditions that in many cases far exceed any existing application. This includes exposure to high-flux deuterium-tritium (D-T) plasmas ($> 10^{24}$ D+T m⁻² s⁻¹), high energy fusion products (e.g. 14.1 MeV n and 3.5 MeV α), impurities, as well as deliberately introduced gas species to promote radiative cooling of the scrape-off-layer. It is not clear that any existing material can satisfy all of the desired performance metrics required for long-term deployment in magnetic-confinement devices, thereby motivating the need for advanced materials and plasma facing component designs [1]. Polycrystalline tungsten has been viewed as a viable starting-point for the ITER tokamak (at present under construction at the Cadarache facility, France), given its high melting temperature, thermal conductivity, and low coefficient of thermal expansion. In terms of its response to plasma exposure, the low sputtering yield and low solubility of hydrogen isotopes in tungsten are also considered advantageous. Nevertheless, conventional polycrystalline tungsten grades suffer from low ductility, and offer only marginal resilience against neutron embrittlement, which may affect their use in higher power reactors. In addition, recrystallized tungsten is also susceptible to inter-granular cracking as a result of transient heat loading and cooling cycles. This could promote crack extension, eventually propagating to the supporting structure [2].

Several strategies have been proposed to improve the properties of tungsten [3-5]. Of particular recent interest is the development of ultra-fine grained (UFG) tungsten materials. A microstructure characterized by tungsten grains < 2 μ m wide may be realized through the incorporation of small transition metal dispersoids to limit grain growth. The dispersoids can suppress recrystallization embrittlement, and the high density of grain boundaries may serve as sinks for displacement damage arising from neutron and high energy ion irradiation [6]. Several efforts are underway to develop and characterize such materials, including recent work led by Kurishita [6-8] and Miyamoto [9]. Their

work focuses on tungsten containing 200 nm diameter TiC (1.1 wt%) or W-TaC (3.3 wt %) dispersoids. Initial testing of the UFG material has demonstrated a lower ductile-brittle transition temperature (240 K). Furthermore, post-mortem analysis of UFG specimens subjected to thermal fatigue loading [10] and thermal shock [11] in electron beam facilities have revealed negligible cracking and surface morphology modification.

While the aforementioned progress is quite promising, optimization of tungsten properties in this manner may affect its performance in other respects. In the present study, we focus on an assessment of (a) plasma-induced surface morphology modification and (b) hydrogen isotope trapping within the material. Because of the low solubility of hydrogen isotopes in tungsten, precipitation of $H_2(g)$ in small, high pressure bubbles and blisters is highly favorable [12]. These structures may grow through a variety of mechanisms, including dislocation loop punching and near-surface crack propagation. This may produce a delaminated layer of material near the surface that is poorly connected to the bulk, and therefore be more susceptible to melting, recrystallization, or flaking during operation. How the modified grain structure of UFG tungsten affects diffusion and trapping of hydrogen isotopes is especially a concern for tritium which, due to its radioactivity, presents a considerable safety hazard if allowed to accumulate within the reactor. Prior investigation of hydrogen-isotope retention in UFG tungsten is limited, and the existing published experimental database for W-TiC contains several contradictory findings. For example, initial high flux plasma-exposures in the PISCES-A linear plasma device revealed very low retention of D within the material compared with pure stress relieved tungsten [9] at an exposure temperature of 300 °C and ion fluence of $5 \times 10^{25} \text{ D m}^{-2} \text{ s}^{-1}$. Later testing by Zibrov et al. [13] conversely revealed consistently higher trapping in W-TiC and W-TaC alloys for fluences ranging between 10^{22} - $10^{25} \text{ D m}^{-2} \text{ s}^{-1}$. Since both studies involved the use of similar materials, the reason for the disparity between these two studies is unclear.

In this work, we seek to identify the physics mechanisms underlying hydrogen isotope trapping and surface morphology changes in UFG W materials. For this purpose, we consider a recently-developed material containing Ti dispersoids to serve as inhibitors to grain growth. This article begins with a description of the material preparation and characterization, along with a discussion of high-

flux D plasma exposures using PISCES-A linear plasma device at the University of California, San Diego. We then present an analysis of the trapped D assessed by thermal desorption spectrometry, followed by a characterization of the plasma-modified surface morphology using several microscopy techniques. Finally, we conclude with an analysis of the material composition using Auger electron spectroscopy and x-ray photoelectron spectroscopy.

II. MATERIAL PREPARATION AND PLASMA EXPOSURE

The ultra-fine grained (UFG) tungsten used in this study was fabricated using a unique power metallurgy process. The raw materials consisting of W and Ti powders were mixed with WC balls and milled using a custom-designed high-energy planetary mill (HEPM) [14] for 6 h. The HEPM process generates a 60 g-force acceleration field that can effectively reduce the crystalline size of tungsten powders to less than 20 nm. After milling, tungsten powders were compacted into 38 mm diameter disc green parts using a uniaxial die press with pressure up to 200 MPa. The green parts were sintered in an atmosphere-controlled tube furnace. The sintering profile include a reduction step at 700-800°C for 3 h in flowing H₂ and a sintering step at 1300 °C for 1 h in Ar. The sintered samples have relative density of about 98% of the theoretical value. The high density achieved at such a low sintering temperature was attributed to the extremely high driving force for sintering in the highly active nano-W powder prepared using the HEPM process. The Ti particles at the tungsten grain boundaries were added as grain growth inhibitors resulting in the ultrafine grain size in the samples.

All of the W-Ti UFG samples prepared for this study were cut to a uniform size of 25 mm diameter, 1 mm thick discs by electrical discharge machining (EDM) and grinding. They were then mechanically polished to an rms surface finish of 10 nm (measured by atomic force microscopy.) For comparison, we also considered two pure tungsten reference materials that are widely used for plasma-exposure studies. The first of these is ITER-grade material (Allied Materials Corp.), where the exposed surface is aligned perpendicular to the rolling direction. This produces a microstructure with grains elongated along the thickness of the material to promote better heat conduction away from the surface. The raw material was in the form of a 25 mm diameter rod, from which 1 mm thick specimens were cut via EDM. Details of the ITER-grade specification may be found in Ref. [15].

Specimens of the second reference material were fabricated from a 1 mm-thick warm-rolled tungsten sheet (PLANSEE), where the microstructure is characterized by grain elongation parallel to the surface. An extensive database is available for each reference material, both of which have far larger grain size than the UFG material described above.

To reveal the basic structure of the UFG material and to enable a more quantitative analysis of grain size, we acquired electron backscattering diffraction (EBSD) maps at five randomly selected locations near the center of the sample surface. A representative selection of the EBSD data is shown in the surface normal projected inverse pole figure-based map depicted in Fig. 1(a). The orientation of the individual grains is conveyed by assigning a red/green/blue colors to each Euler angle, which can be translated to orientations through the adjacent color key. In each case a $15.4\ \mu\text{m} \times 11.5\ \mu\text{m}$ region of the surface was surveyed in a rectangular grid, using $0.1\ \mu\text{m}$ steps. The white regions indicate points where a distinct Kikuchi diffraction pattern could not be resolved. These locations correspond to grain boundaries, where the Ti dispersoids are also present. (Areas of high surface roughness can also lead to indexing errors.) Our attempts to determine the exact phase of the dispersoids using EBSD were ultimately unsuccessful. Since the size of the dispersoids was comparable to the $0.1\ \mu\text{m}$ mapping resolution, this is perhaps not surprising. As will be discussed later in Sec. V, we later found that the Ti particles contained O as well as other impurities, and it is likely that this complex combination of constituents would prevent identification of the exact phase. It is important to note that all orientation data presented in the EBSD maps therefore correspond to tungsten grains. An analysis of the orientations did not reveal any obvious evidence of preferred texture. This is consistent with the powder metallurgy fabrication procedure used, where a random distribution of grain orientations would be expected.

Material microstructure is closely linked not only to the mechanical properties, but also to hydrogen diffusion, trapping, and precipitation within the material. To calculate and interpret the grain size distribution, we used data analysis procedures previously developed by Mingard and co-workers [16] for guidance. We first filtered the EBSD raw data and reconstructed the grain boundaries, using a 10° misalignment threshold. Based on the reconstructed data set, we then calculated the

internal area of the individual grains and then binned them according to their equivalent diameter (d_{eq}), i.e. the diameter of a disc with the same area. The histogrammed grain sizes, presented in Fig. 1(c), are characterized by a large population of small grains, reaching a minimum at $d_{eq} = 0.4 \mu\text{m}$. The distribution then transitions to a broader distribution of larger sizes. As discussed by Mingard et al., this is a characteristic of many metal systems, and the minimum point separating the two parts of the distribution is often used as a cut-off when correcting for small pixel clusters in EBSD maps. Data for grains smaller than $0.4 \mu\text{m}$ are considered questionable due to the resolution limit of the EBSD maps and the presence of the small titanium-oxide dispersoids which interfere with the phase and orientation identification. The effect of varying levels of noise reduction is illustrated by the cumulative distributions shown in Fig. 1(d). Here, pixel clusters of varying size are removed to illustrate the effect on the calculated median grain size. Removing only isolated pixels typically leads to considerable underestimation of the grain size; the use of larger values leads to estimates more consistent with established linear intercept techniques [16]. Using the proposed cut-off value of $d_{eq} = 0.4 \mu\text{m}$ (16 pixels), we estimate the median grain size to be $0.96 \mu\text{m}$. As illustrated in the Fig. 1(c), the portion of the curve corresponding to larger sizes can be fit to a log-normal distribution with satisfactory agreement.

Table 1: Test matrix, including plasma exposure conditions

aterial type	$T_{exposure}$ [°C]	Duration [min]	flux (ϕ) [m ⁻² s ⁻¹]	fluence (F) [m ⁻²]	analyses performed*
rolled sheet	300	60	9.3×10^{21}	3.7×10^{25}	CFM
ITER-grade	300	43	1.5×10^{22}	3.7×10^{25}	CFM
UFG W	200	30	1.7×10^{22}	3.0×10^{25}	FIB, AES
UFG W	300	45	2.2×10^{22}	6.0×10^{25}	EBSD, XPS
UFG W	500	45	2.1×10^{22}	5.7×10^{25}	

*Note: Post-mortem AFM and TDS performed on all specimens.

It is useful to consider this value in the context of other reference tungsten materials. Revisiting our previously published EBSD measurements on ITER-grade tungsten [17], we compiled grain size statistics in a similar manner as described above. Based on this analysis, we estimate $d_{eq} \approx 10 - 20$ μm for the ITER-grade material, considerably larger than what we found in the UFG material.

III. PLASMA EXPOSURE AND ANALYSIS OF TRAPPED DEUTERIUM

To test the response of these materials to high-flux plasma exposure, we used the PISCES-A linear plasma device. This instrument has been used extensively for plasma-materials interaction studies; a more comprehensive description can be found in Ref. [18]. For this series of tests, we secured each specimen to an Inconel target using a Mo nut with a 22 mm aperture. During exposure, the samples were biased to a potential of -100 V. A small correction to the bias voltage using the plasma space potential can be taken into account to calculate the incident ion energy (typically 5-8 eV.) Using reciprocating Langmuir probes, we characterized the flux incident upon the target at 15 min. intervals. The exposure temperature was measured using a thermocouple pressed against the back of each sample. In general, the desired specimen temperature could be reached by using the target cooling flow rate as a coarse adjustment, while modifying the plasma parameters for finer

control. With this in mind, there was some modest variability in plasma parameters between tests.

Using this approach, the sample temperature stabilized within 5-10 minutes of exposure and could be controlled to within ± 20 °C of the desired set point. The test matrix used in this study is provided in Table 1.

The same optical furnace described previously for sample annealing was also employed for thermal desorption. The desorbed species were characterized via a 300 amu quadrupole mass analyzer (QMA), with the $m/q = 4$ signal calibrated using a variable flow D₂ capillary ($\pm 7\%$ accuracy.) During thermal desorption, each sample was heated at a constant rate of 0.54 °C/s from room temperature to 1000 °C over a 30 min interval. We maintained this temperature for 15 min. afterward to ensure complete desorption of hydrogen from the material. The measured thermal desorption spectra are plotted in Fig. 2 as a function of time, with the period of linear temperature increase to 1000 °C indicated by the dashed lines. The top axes show the corresponding temperature.

In Fig. 2(a) – (c), desorption spectra from the UFG tungsten specimens (exposure temperatures: 200 – 500 °C). As can be seen, the peak desorption rate for the UFG tungsten progressively shifts to higher temperatures as the exposure temperature increases. It is also interesting to note the onset of desorption occurs at approximately the same temperature as the plasma exposure, as indicated by vertical solid line in each case. This can be understood in the context of how hydrogen diffuses into the W material and binds to a range of defects at different energies. Hydrogen that is only weakly bound to defects will be released at low temperatures. Such defects will not be populated with hydrogen if the material is exposed to a processing step (e.g. plasma exposure) at much higher temperature. Further details on the equilibrium fraction of defects populated by hydrogen may be found in recent work by Wampler and Doerner [12]. To the right, desorption spectra for each of the reference samples exposed at 300 °C are shown in panels (d) and (e). The basic behavior observed here is comparable to other studies in the literature [19]. When comparing the desorbing flux from the reference samples exposed at 300 °C with the UFG material exposed under same conditions, it is evident that the release of D from the W-Ti material is higher at nearly all temperatures. The integrated total was a factor of 3 higher in the UFG tungsten compared with the conventional

polycrystalline material. In comparing the shape of the desorption signals from the UFG material and reference specimens, it was not possible to distinguish any specific peak associated with release from the dispersoids.

It is also worthwhile considering the total trapping of D within the material determined from the TDS in the context of the available literature database. Fig. 3 compares the work presented in this article with other published studies. In panel (a), we show the temperature dependence of D retention between 50 °C – 550 °C. For comparison, we include plasma exposure data by Alimov et al. [20], Causey et al. [21], and our prior work using the Tritium Plasma Experiment [17], as well as high-flux ion beam measurements by Orogodnikova [22]. In each case, the fluence is indicated, as well as the material grade considered (ITER-grade, “I”; rolled plate, “R”; re-crystallized, “X”.) The general trend portrayed by these data is a gradual increase in retention, reaching a maximum at 250 °C. The retained D quickly decreases at higher temperatures, and is only moderately dependent on fluence. Our measurements for the UFG tungsten, highlighted by the solid markers, follow this same general trend, and are comparable in magnitude compared with established database. While the dependence of retention on fluence was not directly addressed in this work, it is still useful to see how our data fits with trends observed in prior studies. Fig. 3(b) shows experimental data from Zibrov et al. in Ref. [13] for W-TiC and W-TaC materials at 327 °C. For reference, we also include the high-flux W-TiC data from Ref. [9], as well as retention measurements from the present study. Here we include the W-Ti material at 200 °C and 300 °C, as well as the pure-W grades.

IV. MICROSCOPY OF PLASMA-EXPOSED SURFACE

Another aspect of assessing the compatibility of nanostructured tungsten with fusion plasmas is the extent of surface modification caused by the exposure. To characterize morphology changes, we examined the surfaces using an Olympus LEXT OLS4100 confocal microscope (CFM). This instrument enables rapid scanning of large sample areas. For detailed scans of the UFG material where better resolution was desired, we used a Digital Instruments Nanoscope IIIa atomic force microscope (AFM.) Because the tip diameter (5-10 nm) was much smaller than the surface features

being measured (~ 100 nm), convolution artifacts could be safely neglected. We acquired surface maps at three randomly selected areas for each specimen.

The posttest surface morphologies are illustrated by the surface height maps in Fig. 4, with panels (a) and (b) corresponding to the PLANSEE (rolled plate) and ITER-grade specimens, respectively. The coloration corresponds to the height scale below each figure. Because the two reference materials contained prominent surface features corresponding to near-surface blisters, we scanned a relatively large $100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ region for each. In the case of warm-rolled W, large blisters are clearly visible. This is consistent with prior findings [23], and is indicative of delamination at near-surface grain boundaries. The elongation of the grains parallel to the surface provides an interface for this delamination to occur. Blisters are also present on the surface of the ITER-grade tungsten, though they are much less pronounced. As discussed in Ref. [21], bubbles and blisters within the ITER-grade material tend to form within individual grains. Conversely, neither optical nor atomic force microscopy revealed the presence of large-scale blisters or bubbles on the surface of the UFG tungsten material after plasma exposure. The more detailed height map from the ultra-fine grained tungsten shown in panel (c) depicts a surface that is quite smooth, with only small depressions 100-200 nm in depth. (Note the change of lateral scale: image (c) shows a $10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$ area.) These features were not present immediately after mechanical polishing, where AFM analysis revealed an rms roughness of 10 nm. Scanning electron microscope images indicate that these changes occur after annealing, rather than after plasma exposure. Even in the more detailed AFM maps, we found no evidence of bubble or blister formation. Furthermore, we noted no obvious dependence of surface morphology on sample exposure temperature.

Fig. 5 depicts a post-mortem scanning electron microscope image of a cross-section of the UFG tungsten. The surface depicted here had been held at 200 °C during plasma exposure, corresponding to the desorption profile shown in Fig. 2(a). The focused ion beam (FIB) cut was performed using a Ga ion beam. Prior to milling the cross-section, a thin layer of Pt was first deposited onto the surface through electron beam evaporation, followed by ion beam deposition. As a result, the protective Pt coating consists of two different microstructures, as is apparent in Fig. 5(b). Once the cut was

completed, the resulting cross section was then imaged at 52° relative to the surface normal. This causes the aspect ratio of the cross section to be distorted due to the angle of tilt. Immediately apparent from the cross-section is the presence of the Ti dispersoids, which appear as darker colored grains. Near the surface, these dispersoids are slightly recessed, consistent with our AFM measurements. A possible cause of this texturing is that annealing serves to relieve stress in the W surface produced by mechanical polishing. Typically hydrogen precipitate growth (via dislocation loop punching or other mechanisms) results in deformation of the nearby surface. Within the resolution of our electron microscopy (~30 nm), we noted no evidence of any such defects formed within the material.

V. COMPOSITION ANALYSIS

Impurities contained within the bulk material, even at trace concentrations, may affect trapping of hydrogen isotopes. To examine the composition of the near-surface, we used Auger electron spectroscopy (AES) to analyze a fragment of the W-Ti specimen that had been exposed at 200 °C. To perform the analysis, the sample was loaded into a vacuum system capable of a base pressure $< 10^{-10}$ Torr. Using a 500 eV Ar⁺ ion beam, we prepared the surface by sputtering impurities that had chemisorbed due to air exposure. It was possible to focus the electron beam used for AES analysis to a spot size $< 0.2 \mu\text{m}$ in diameter, thereby enabling independent analysis of the small Ti grains and the W matrix. In Fig. 6, we show Auger spectra obtained for both of these areas using the standard convention of presenting the derivative spectra to emphasize the location, shape, and size of the Auger peaks.

The AES spectrum in panel (a) is from a W grain. With the exception of C and O, all peaks are associated with W. The presence of O and C is not surprising, particularly since CO is a common vacuum impurity and the sputter cleaning had occurred more than 2 days prior to obtaining these spectra. In the case of the Ti dispersoids, the AES spectrum is more complex. As one would expect, the most prominent peaks are associated with Ti, as shown in panel (b). However, there is a comparable amount of O (28.9 % at.) in the particle as Ti (25.9 % at.), and more than an order of magnitude more O than on the surrounding W surface (1.6 % at.) In addition to the O, we noted a

group of Auger peaks at electron energies between 300 eV and 750 eV. This corresponds to the shaded region in Fig. 6(b), and is highlighted at an expanded scale in the inset. In addition to Ti, we noted both Fe (10.1 % at.) and Cr (23.5 % at.) impurities. Because these species are contained in steels, it is plausible that these constituents were incorporated into the material during fabrication, or existed as impurities within the raw material. A small amount of W (11.6 % at.) accounted for the remaining portion of the dispersoid composition.

In addition, we performed X-ray photoelectron spectroscopy (XPS) to gain greater clarity into how oxygen binds to the various constituents of the dispersoids. We used X-rays produced by a Mg K α X-ray source to analyze a 0.8 mm diameter area near the center of the UFG specimen previously exposed at 300 °C. XPS spectra were acquired with a hemispherical analyzer (Physical Electronics), attached to a vacuum chamber maintained at a base pressure of 10^{-9} Torr. Because of the larger spot size, it was not possible to independently analyze the dispersoids and the W matrix as was the case with the AES measurements. For depth profiling, we used a 3 keV Ar $^{+}$ beam rastered over a 2 mm $\times$ 2 mm surface area that overlapped with the incident X-ray spot; the corresponding sputtering rate was estimated to be 10.1 nm/min. With the exception of Cr, photoelectron peaks associated with all previously identified species were also found with an XPS survey scan. Additional Ar $^{+}$ sputtering of the surface did not reveal any evidence of Cr buried within the material. It is conceivable that instrument sensitivity could account for absence of Cr from the XPS spectra, particularly since the electron beam used for AES could be focused onto individual dispersoids where the Cr was localized.

Chemical binding information is typically determined from XPS based on chemical shifts in the photoelectron line positions in comparison with reference spectra obtained using a pure material. We acquired high-resolution energy scans to resolve these shifts, as shown in Fig. 7. Scans were obtained after intervals of Ar $^{+}$ sputtering totaling 5 s, 30 s, and 60 s in duration. First, consider the photoelectron lines associated with C, a common impurity found on surfaces after air exposure. The structure of the associated photoelectron lines evolves during Ar $^{+}$ sputtering, suggesting contributions from both chemisorbed species and impurities within the bulk. The position of the C lines prior to sputtering initially appears consistent with graphite, but then shifts to lower energy (WC) after Ar $^{+}$

sputtering. While WC may indeed be present within the bulk material, it is important to keep in mind that it could also be an adventitious effect of recoil implantation of C into W during Ar^+ sputtering [24].

An analysis of the Ti 2p photoelectron lines shown in Fig. 7 indicates that the Ti in the dispersoids is bound to O in the form of TiO_2 . After 5 s exposure to the Ar^+ ion beam, the XPS spectrum remains consistent with TiO_2 , indicating that O binds to the dispersoid throughout, rather than being present only at the surface. Further sputtering appears to remove the Ti. Given the shallow sputtering depth considered here, the most likely explanation is preferential removal of the Ti. Conversely, the initial XPS spectrum appears consistent with Fe_2O_3 , but then shifts to pure Fe after sputtering. (Peak fitting analysis indicates a ~30% of the signal is still oxide after 60 s of sputtering.) Barring any artifacts introduced by the Ar^+ beam, this indicates that the Fe exists at least partially as pure metal within the dispersoids. The W 4f lines are initially characterized by additional structure associated with WO_3 . After sputter cleaning, the structure associated with the oxide disappears, indicating that it was present only at the surface.

VI. DISCUSSION AND CONCLUDING REMARKS

As discussed in the previous sections, our TDS analysis indicates that approximately 3 times more D became trapped in the UFG W than the conventional polycrystalline tungsten grades. This is consistent with prior observations by Zibrov et al. [13], who found similar behavior for W-TiC and W-TaC, but differs from prior measurements by Miyamoto et al. [9]. The reason for this discrepancy is unclear, given that both our work and the measurements of Miyamoto and co-workers were performed using PISCES-A using similar exposure conditions. A possible explanation could be subtle differences between the UFG tungsten used in the two tests, or some other aspect of the plasma exposure not taken into account here.

As can be seen from Fig. 2, the main peak in the TDS spectrum for UFG W is considerably broader than what was observed for the reference material at 300 °C. One possible explanation for this behavior is that a wider distribution of traps is present in this material [25]. One obvious difference is

that the UFG tungsten contains a much higher density of grain boundaries. In parallel with this study, additional measurements have been undertaken to assess high-temperature gas-driven permeation rates through UFG tungsten. (For further details, please see Ref. [26].) At low temperatures, moderately higher permeability of UFG material was observed in comparison with ITER-grade W. However, the difference between the two materials gradually diminishes as the temperature approaches 1000 °C. In Ref. [26] it was proposed that grain-boundary diffusion contributes to the higher permeability; it is conceivable that such an effect could similarly be in effect during plasma exposure as well. There is also some theoretical support for this mechanism from kinetic Monte Carlo simulations [27]. Enhanced diffusion along grain boundaries could facilitate migration of D to deeper trap sites within the material; this would also contribute to broadening of the thermal desorption peaks. Furthermore, it is conceivable that the grain boundaries themselves may serve as trapping sites for hydrogen. Such an explanation would be consistent with recent observations by Lindig et al. [28], who used nano-scale secondary ion mass spectrometry (nano-SIMS) to map the lateral distribution of hydrogen retained in recrystallized tungsten exposed to plasma at 97 °C. This analysis provided evidence of elevated H concentrations at grain boundaries as well as within near-surface precipitates. A wide range of trapping energies may be associated with grain boundaries depending on the orientation mismatch between adjacent grains. This would also be expected broaden the TDS spectra. A more systematic study of the effects of grain boundary density on hydrogen trapping would be a worthy avenue of further study.

An issue that must be resolved is the contribution of additional trapped D within the dispersoids. Whereas Ti metal has a strong affinity for H isotopes (and under appropriate conditions forms a hydride), TiO₂ passivates the surface and presents a strong barrier to hydrogen ingress. Concentration profiles in single crystal TiO₂ exposed to T₂(g) were measured using autoradiography by Caskey [29] for temperatures between 155 – 300 °C. As confirmed by other researchers using electrochemical cells at ~ 25 °C [30], the diffusion rate of H in the bulk is considerably lower in TiO₂ than in pure Ti by a factor of 10² – 10⁴, and even lower than W at comparable temperatures. Based on this, as well as the low solubility of H in other oxide materials [31], it seems reasonable that ingress of D into the

dispersoids would be minimal, and their contribution to retention in the UFG material would be modest. However, this analysis does not account for other trapping by other impurities present in the dispersoids or within the TiO_2 itself. In addition, while the XPS analysis confirmed that the electronic structure is consistent with TiO_2 , the Auger analysis indicates that the O and Ti are present in the dispersoids at relatively equal concentrations. This suggests that the Ti dispersoids may not be fully oxidized to TiO_2 . To definitively address these questions, further analysis using characterization tools that map the local distribution of H in the surface, such as nano-SIMS is recommended.

A fundamental question is: How significant is the three-fold increase in retention that we observed? In general, tungsten performs well from a tritium inventory perspective, so a modest trade-off here may be tolerable if the material can be optimized for considerable improvements in other respects. As illustrated by Fig. 2, the retention exhibited by the UFG tungsten tested here is still within the spread of values contained within the experimental database for pure W.

In contrast to the ITER grade and warm-rolled reference materials, the UFG tungsten showed very little change in surface morphology as a result of plasma exposure, including no evidence of large-scale blistering or bubble growth. Furthermore, within the resolution of our SEM (~ 50 nm), no obvious pores or voids in the bulk material were evident in the focused ion beam cross sections. In many respects this is a positive finding, as regions of the surface that have delaminated from the bulk contribute to the degradation of the surface, contribute to dust formation, and are more susceptible to melting during transient heat loading.

Based on these analyses, it is reasonable to conclude that UFG W materials merit further consideration for use as plasma-facing materials, and our preliminary work does not identify any insurmountable obstacles to their success. With this in mind, it is worth considering a strategy to more fully test how these materials would respond under a more realistic environment of a large reactor environment. The moderate temperatures considered here (< 500 °C) are not likely to be high enough to provide an evaluation of how the UFG material will perform during transient heat loads. For example, after exposure of W-TiC samples to 31 ohmic discharges in the limiter lock system of the TEXTOR tokamak, Ueda and co-workers [32] observed enhanced erosion of TiC precipitates at

temperatures above 1150 °C. Sputtered or evaporated material could present a source of impurities for the tokamak plasma; it is unclear whether TiO₂ would behave in the same manner. Furthermore, it is important to note that the plasma exposures performed here included moderate fluences for easy comparison with the existing experimental database. Testing at higher fluences, particularly in excess of 10²⁷ D m⁻² would be valuable for identifying any unforeseen effects.

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FIGURE CAPTIONS

FIG. 1: Summary of EBSD analysis, including (a) surface normal projected inverse pole figure-based map of the UFG surface, and (b) color key showing relationship to orientations. A histogram of grain size distributions is shown in (c), along with a log-normal fit. The median grain size may be determined from cumulative grain size distributions (d), calculated here for varying levels of noise reduction. All grain sizes are calculated in terms of the diameter of an equivalent circle (d_{eq}).

FIG. 2: Thermal desorption spectra from tungsten specimens after exposure in the PISCES-A linear plasma device. The plots at the left (a-c) correspond to UFG W at varying exposure temperature. The top axis conveys the sample temperature during heating; the beginning and end of the heating cycle is denoted by the dashed lines. The onset of the main D_2 release peak appears to correlate roughly with the exposure temperature, as indicated by the vertical solid lines. For comparison, the plots at the right show the desorption profiles from ITER-grade (d) and PLANSEE rolled sheet (e) reference materials at an exposure temperature of 300 °C.

FIG. 3: Variation of trapped D with temperature (a) and fluence (b) are shown. In panel (a), the comparison with the literature database [17, 20-22] includes studies performed over a range of fluences. For each study, the material used is indicated by “I” (ITER-grade), “R” (rolled plate), or “X” (re-crystallized). For the fluence dependence depicted in panel (b), a comparison is made with Zibrov’s [13] and Miyamoto’s prior work [9].

FIG. 4: Representative AFM and CFM surface height maps for (a) rolled W sheet, (b) ITER-grade W, and (c) UFG tungsten. Note the difference in height scale for each map, as well as the different lateral dimensions for the UFG material in panel (c).

FIG. 5: SEM images of the UFG W showing (a) the top surface, and (b) a cross-section created by focused ion beam profiling. The darker regions of the surface correspond to Ti grains.

FIG. 6: AES spectra for the (a) W matrix as well as the dispersoids (b). The locations of peaks associated with prominent surface species are highlighted by vertical lines. The inset shows an expanded view of the shaded region of panel (b) (corresponding to an electron energy range of 300 eV – 750 eV.)

FIG. 7: XPS data showing photoelectron peaks associated with the various constituents of the UFG material. The arrows represent established peak locations for the pure material, whereas the dashed lines indicate offsets associated with carbide or oxide formation. The vertical scale is in arbitrary units.