

## W erosion due to low energy O<sup>+</sup> and D<sup>+</sup> impact

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### Abstract

The erosion of polycrystalline tungsten by 0.15–10 keV D<sub>3</sub><sup>+</sup>, O<sub>2</sub><sup>+</sup> and Ar<sup>+</sup> has been studied at temperatures of 300–1900 K, using line-of-sight quadrupole mass spectroscopy (LOS-QMS) and mass-loss measurements. The overall rates of erosion at 300 K are consistent with standard Monte Carlo calculations (TRIM 2000), indicating that physical sputtering is the process dominating erosion. During simultaneous bombardment by 500 eV/D<sup>+</sup> and 75 eV/O<sup>+</sup> the mass-loss due to bombardment by D<sup>+</sup> appeared to be unaltered by the addition of O<sup>+</sup>. During O<sup>+</sup> bombardment the LOS-QMS signals show clear peaks at masses 184 (W) and 200 (WO). These peaks are significantly larger during 5 keV/O<sup>+</sup> bombardment than during 10 keV Ar<sup>+</sup> bombardment, indicating the presence of a chemical component of erosion by O<sup>+</sup> ions. This chemical component is estimated to be <10% of the physical sputtering yield for 5 keV/O<sup>+</sup>. The ‘chemical erosion’ process is fairly complex: it is sensitive to the composition of the surface; the yield (mass 184 net peak height divided by the O<sup>+</sup> flux) decreases with decreasing O<sup>+</sup> energy; it has an apparent threshold energy of 350 eV/O<sup>+</sup>, which suggests that bond-breaking or displacement creation is involved; the yield decreases with increasing O<sup>+</sup> flux and temperature; and the yield generally decreases when D<sup>+</sup> is incident on the W simultaneously with the O<sup>+</sup>.

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### 1. Introduction

Tungsten is a prime candidate for use as a plasma-facing material in the divertor in next-step fusion devices such as ITER [1]. It will be exposed to high fluxes of hydrogen isotopes, primarily D and T, He ash, and smaller fluxes of impurities, such as Be, C and O. It seems likely that the rate of erosion of the tungsten surfaces will be dominated by these impurity fluxes, as long as the hydrogen fluxes do not result in extensive blistering and exfoliation, and in the absence of extensive melting caused by disruptions or vertical displacement events. This erosion may have a major impact on component lifetime, plasma purity and fuel recycling. This study has been undertaken to identify the syner-

gistic effects of bombardment of tungsten by deuterium and oxygen ions over a range of tungsten temperatures (300–1900 K), ion energies (0.15–10 keV) and ion fluxes (10<sup>18</sup>–10<sup>20</sup>/m<sup>2</sup> s).

Tungsten sputtering by oxygen was measured by Hechtel et al. [2,3] as a function of target temperature and ion energy, using mass-loss measurements. These experiments were performed in three different accelerator systems, and produced sputtering yields that varied by as much as an order of magnitude, apparently due to variations in the surface composition. The results from experiments with tungsten at 1900 K were in good agreement with their TRIM.SP calculations [3] for physical sputtering of a clean W surface by O<sup>+</sup>. At lower temperatures, the calculations were made to match the data by increasing the oxygen content of the surface.

Of interest for ITER is whether deuterium erosion rates will be affected by small amounts of impurity ions. Roth et al. [4] suggested that the addition of sufficient oxygen resulted in the sputtering of WO<sub>x</sub> molecules,

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with lower surface binding energies, shifting the deuterium sputtering threshold to lower energy. They observed sputtering by  $D^+$  (in the presence of  $10^{-2}$  Pa of  $O_2$  gas) at energies below the threshold of  $300 \text{ eV}/D^+$ . The sputtering yields for these oxidised W targets were very small,  $\approx 2 \times 10^{-4} \text{ W}/D^+$ , but significantly higher than observed without the addition of  $O_2$ . Above the threshold energy, the addition of  $O_2$  appeared to *reduce* the sputtering yield, which is similar to the results of Hechtl et al. [2,3] for  $O^+$  sputtering of W.

In contrast, Hirooka et al. [5] estimated the *effective* net erosion of W at 1773 K during plasma bombardment, using spectroscopic methods calibrated by mass-loss measurements. In this case, the plasma was primarily hydrogen, with up to 2% oxygen. The erosion yields measured were roughly consistent with the sum of the expected physical sputtering yields due to  $D^+$  and  $O^+$ . Hirooka et al. [5] calculated the expected W loss due to the evaporation of volatile tungsten oxides, using the results of Wu's calculations [6], and found that this component should be roughly 0.6% of the observed erosion rate. As a check, Hirooka et al. [5] compared the erosion yields for 400 eV ions at 773 K and at 1273 K, and found that there was no temperature effect on the erosion rate, indicating that the evaporation of volatile oxides was not a significant factor.

In the current experiments we further investigate  $O^+$  sputtering of W, and also examine the combined effect of  $75 \text{ eV}/O^+$  and  $500 \text{ eV}/D^+$  on the sputtering of W, using a dual-beam accelerator.

## 2. Experiment

### 2.1. Specimens

The specimens are  $25 \mu\text{m}$  thick polycrystalline tungsten foils (from Rembar Corporation) cut into strips of approximately  $10 \text{ mm} \times 40 \text{ mm}$ . According to the supplier, the material is 99.95 at.% pure W; the major impurities are Mo (<100 appm), C (<30 appm) and O (<30 appm). The H content was <5 appm. The foils were hot-rolled, annealed to relieve stress, and etched by the manufacturer in a proprietary process.

### 2.2. Facility

The UTIAS dual-beam facility [7] is currently set up for simultaneous implantation by two ion species: one from a duoplasmatron ion source, mass-analysed through a  $30^\circ$  sector magnet, with energies of 1.0–10 keV; and another from a hollow cathode ion source, mass-analysed through a  $90^\circ$  sector magnet, also with energies of 1.0–10 keV. The ion beams are each incident on the target at an angle of  $21^\circ$  to the surface normal, thus forming a  $42^\circ$  angle between the two beams. A

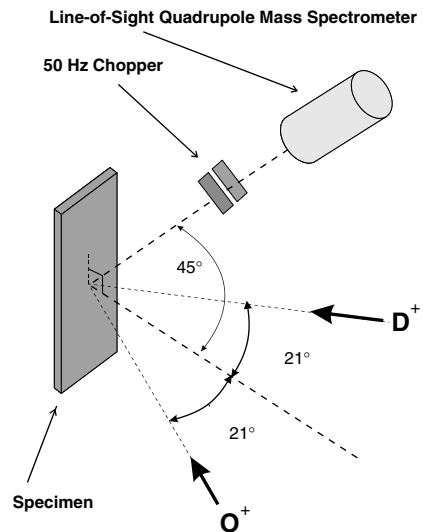


Fig. 1. Schematic diagram of the arrangement of the specimen with respect to the two ion beams and the quadrupole mass spectrometer.

schematic diagram of the arrangement of the specimen with respect to the two ion beams and the quadrupole mass spectrometer is shown in Fig. 1. The specimen is clamped between stainless steel jaws, and can be heated by direct current to temperatures of up to 2000 K, as measured by an IRCON model 300 infrared pyrometer, previously calibrated for a W foil specimen using a W/Re thermocouple. Secondary electron suppression is accomplished by biasing the target to at least +30 V, to enable accurate measurement of ion beam currents on the target. Ion beam energies can be lowered by increasing the target bias up to 1000 V, without significantly defocusing the beam as long as the net ion energy is 150 eV or higher. Beam spot sizes are typically 3–5 mm in diameter, and particle fluxes range from  $10^{18}$  to  $10^{20}$  ions/ $\text{m}^2 \text{ s}$ . The base vacuum is  $<3 \times 10^{-6}$  Pa, and the operating pressure is about  $2 \times 10^{-5}$  Pa due to gas from the ion sources. In these vacuum conditions, the surface would be exposed to one monolayer (about  $10^{19}/\text{m}^2$ ) of oxidizing gases ( $H_2O$ , CO,  $O_2$  and  $CO_2$ ) in approximately 30 s. The sticking coefficient would be highly dependent on the surface composition, varying from about 0.5 for a clean W surface to as low as 0.001 for an oxidized surface [8].

### 2.3. Procedure

The effects of the ion bombardment of W are determined by two primary analysis techniques. One is line-of-sight quadrupole mass spectroscopy (LOS-QMS), in which the emitted particles from the target surface pass through a 50 Hz chopper on their way to a Faraday

plate collector in an Extranuclear Quadrupole Mass Spectrometer, modified with a blocker plate to minimize the transmission of reflected ions (chemical effects from sputtered  $\text{WO}_x$  prevent the use of an electron multiplier). The background noise is reduced using a lock-in amplifier. The other technique is mass-loss measurement – determining the sputtering yield by measuring the mass of the foil before and after ion bombardment. The latter is made with a Mettler-Toledo AG285 microbalance with a precision of  $\pm 0.01$  mg. The mass of the W specimen is about 200 mg. The mass-loss measurements were made *ex vacuo*: the chamber was vented to air to change samples after each implant.

### 3. Results and discussion

#### 3.1. W erosion due to $\text{O}_2^+$ using mass-loss measurements

W foil specimens were weighed before and after bombarding with 10 keV  $\text{O}_2^+$  ions (i.e., 5 keV/ $\text{O}^+$ ) at 300 K with fluxes of about  $10^{19}$   $\text{O}^+/\text{m}^2\text{s}$ , to fluences of up to  $3 \times 10^{23}$   $\text{O}^+/\text{m}^2$ . (Here we designate the two O atoms in the  $\text{O}_2^+$  molecular ion by  $\text{O}^+$  even though the  $\text{O}_2^+$  ion is only singly charged; similarly  $\text{D}^+$  represents the D atoms in the  $\text{D}_3^+$  molecular ion.) The resultant sputtering yield is 1.0 ( $\pm 0.2$ ) W atoms removed per incident  $\text{O}^+$ , which is in good agreement with TRIM 2000 [9] calculations for a surface containing about 5 at.% oxygen. However, this value is somewhat larger than the value of 0.69 calculated by Hechtl et al. [3] for pure W (using TRIM.SP, a modified version of TRIM, by Aratari and Eckstein [10]). The difference is attributed to different stopping powers: TRIM 2000 uses newer data. Varying the distribution of oxygen near the surface changes the TRIM calculated sputtering yield of W from 1.15 for oxide-free W to 0.55 for a surface layer of WO. (By comparison, 10 keV  $\text{Ar}^+$  ions resulted in a sputtering yield of 3.4 (measured by mass-loss), also in good agreement with TRIM.) The good agreement with physical sputtering calculations implies that physical sputtering is the dominant erosion process, i.e., any chemical effect is less than the uncertainty caused by variations in surface composition. SIMS analysis showed an even distribution of surface impurities, with no significant change in impurity distributions at the grain boundaries of either an unimplanted W specimen, or the W specimen implanted with 5 keV  $\text{O}^+$  ions to a fluence of  $10^{22}$   $\text{O}^+/\text{m}^2$  – corresponding to  $>10$  nm erosion. SIMS depth profiling indicated that the implanted oxygen diffused well beyond the range of the ions.

Fig. 2 shows the sputtering yields of W as a function of energy, determined by mass-loss measurements in the current set of experiments (solid circles), compared to TRIM 2000 calculations (solid line) and Hechtl et al.'s experimental data for sputtering of W by  $\text{Ne}^+$  (open

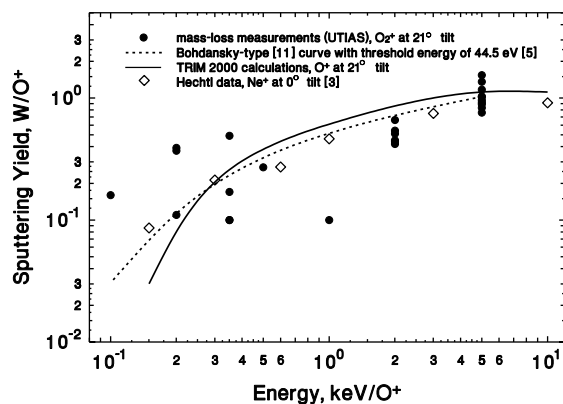


Fig. 2. Sputtering yields as a function of energy for  $\text{O}_2^+$  incident on W at 300 K, from mass-loss measurements, with the ion beam incident at  $21^\circ$  to the normal. Experimental data for  $\text{Ne}^+$  sputtering (open diamonds [3]), TRIM 2000 [9] calculations, and a Bohdanský-type [11] curve fit to the experimental data are shown for comparison.

diamonds). Ne is similar in mass to  $\text{O}^+$  but does not oxidize the surface. Note that, in the current experiments, the W specimens were implanted at  $21^\circ$  to the normal; the TRIM 2000 calculations are for pure W surfaces, also tilted at  $21^\circ$ . The dashed line is a fit to the experimental data following the revised Bohdanský equation for sputtering [11], using a threshold energy of 44.5 eV [5]. There is considerable scatter in the experimental data, most probably due to variations in the surface impurity concentrations. It can be seen that the data from the current set of experiments are in fairly good agreement with TRIM 2000 calculations and follow the Bohdanský-type equation reasonably well.

Further TRIM 2000 calculations indicate that the surface oxygen content should vary with ion energy, because the relative sputtering yields of oxygen and tungsten vary with energy. For example, TRIM 2000 predicts that 0.5 keV  $\text{O}^+$  incident on W at  $21^\circ$  to the surface normal would result in a reflection coefficient of 0.19, and sputtering yields of 1.09 O atoms/ $\text{O}^+$  and 0.14 W atoms/ $\text{O}^+$  for a steady-state composition of 32% W, 68% O (determined by iterative TRIM calculations, varying the composition). By comparison, for 5 keV  $\text{O}^+$ , the steady-state composition should be about 60% W and 40% O in the near-surface region (reflection coefficient of 0.27, and sputtering yields of 1.16 O atoms/ $\text{O}^+$  and 0.65 W atoms/ $\text{O}^+$ ). The steady-state composition should be achieved by the time the  $\text{O}^+$  bombardment has eroded through one mean ion range, 7.2 nm for 5 keV  $\text{O}^+$  and 1.8 nm for 0.5 keV  $\text{O}^+$ . This would have occurred after a fluence of about  $4 \times 10^{20}$   $\text{O}^+/\text{m}^2$ , less than 1% of the total fluence in the mass-loss experiments. These calculations assume that the only significant loss of oxygen from the surface is due to physical

sputtering. If there is oxygen diffusion away from the implant area across the specimen surface, or release of oxygen through recombination or volatile oxide formation, the surface concentration of oxygen would be lower. The fact that the erosion yields obtained in the current experiments generally agree well with the TRIM 2000 calculations for clean W surfaces suggests that some oxygen is removed from the surface by means other than physical sputtering.

### 3.2. W erosion due to simultaneous $O_2^+$ and $D_3^+$ impact using mass-loss measurements

#### 3.2.1. Relatively high energy $D_3^+$ and $O_2^+$

Bombarding W with 9 keV  $D_3^+$  (i.e., 3 keV/ $D^+$ ) resulted in a sputtering yield of  $0.020 \pm 0.004$ , in good agreement with TRIM 2000 calculations (0.017), although higher than the value of 0.010 calculated using TRIM.SP [12], and the experimental value of 0.006 observed by Roth et al. [13]. Again, the experimental differences are attributed to differing surface composition. The differences between TRIM 2000 and TRIM.SP calculations are presumed to be due to the use of different stopping powers.

Bombarding simultaneously with both 5 keV/ $O^+$  and 3 keV/ $D^+$ , at flux ratios of 0.33  $O^+$ / $D^+$  and 0.14  $O^+$ / $D^+$ , resulted in the same sputtering yield as observed when bombarding with only 5 keV  $O^+$ , i.e., 1.0 ( $\pm 0.2$ )  $W/O^+$ . This implies that the addition of the  $D^+$  flux does not have a significant effect on the  $O^+$  erosion yield, i.e., the effect is  $<10\%$ . This is consistent with physical sputtering predictions.

#### 3.2.2. Relatively low energy $D_3^+$ and $O_2^+$

Next, we performed experiments with  $D^+$  and  $O^+$  energies similar to those used by Hirooka et al. [5]. (Note: we are using  $D^+$  and  $O^+$  beams whereas Hirooka et al. used a deuterium plasma containing up to 2% oxygen.) First,  $D^+$ -only irradiation of W was performed using 1.5 keV  $D_3^+$  (500 eV/ $D^+$ ) at 300 K and at 1000 K, with fluxes of  $3\text{--}5 \times 10^{19}$   $D^+/m^2 s$ . The energy was the lowest for which it was possible to obtain sputtering yields large enough to be measured in a reasonable time. The erosion yields were identical for both temperatures,  $6 (\pm 3) \times 10^{-3}$   $W/D^+$ , but larger than the  $2.3 \times 10^{-3}$   $W/D^+$  value predicted by Eckstein and Laszlo [12]. Guseva et al. [14] measured an even smaller yield of  $1.2 \times 10^{-3}$ , and Roth et al. [13] measured a yield of  $7 \times 10^{-4}$ . It is not clear why the sputtering yields vary so much, although it seems likely that surface layer composition is critically important, and varies under different experimental conditions.

Simultaneous bombardment with 500 eV/ $D^+$  and 75 eV/ $O^+$ , with  $O^+$ / $D^+$  flux ratios varying from 1% to 11%, resulted in erosion yields identical to the  $D^+$ -only cases, i.e.,  $6 \times 10^{-3}$   $W/D^+$ , as would be expected if physical

sputtering was the dominant erosion process. This observation is consistent with those reported by Hirooka et al. [5]. Had there been a decrease in the surface binding energy of the W due to the addition of  $O^+$ , the sputtering yield would have increased. (The  $O^+$  energy of 75 eV was chosen so that the physical sputtering by  $O^+$  would be significantly less than that by the much higher fluxes of  $D^+$ . Roth et al. [4] calculated this yield as  $8 \times 10^{-3}$   $W/O^+$  for an oxidized W surface.) In our present experiments the  $O^+$  (ion) flux at the specimen surface was 3–30 times greater than the thermal flux of oxidizing molecules ( $O_2$ ,  $H_2O$ ,  $CO$ ,  $CO_2$ ) due to background gas, mostly from the ion source; hence, the effect of the background gas is considered to be negligible. It can be concluded that any chemical effect resulting from the added  $O^+$  to  $D^+$ -only irradiation was less than the uncertainty in the mass-loss measurements, i.e., less than 50% of the physical sputtering by the 500 eV/ $D^+$ .

### 3.3. W erosion due to single beam $O_2^+$ and $Ar^+$ impact using LOS-QMS measurements

LOS-QMS data were collected for W foil specimens at 300 K during bombardment by either 10 keV  $Ar^+$  or  $O_2^+$  at energies of 0.3–10 keV (0.15–5 keV/ $O^+$ ). Examples of these spectra are shown in Fig. 3. (Note that the QMS has been tuned for maximum sensitivity at about mass 184, and the sensitivity as a function of mass has not been calibrated.) The highest mass detectable was estimated to be mass 250. Although no peaks at masses greater than 200 were observed, this does not necessarily mean the absence of higher-mass volatiles, e.g.,  $WO_2$  (mass 216) or  $WO_3$  (mass 232). The cracking patterns of tungsten oxides in the QMS ionizer are not known, so it is possible that some portions of the W and WO peak yields observed were due to fragments of heavier oxides which broke up under electron bombardment in the QMS ionizer. Attempts were made to

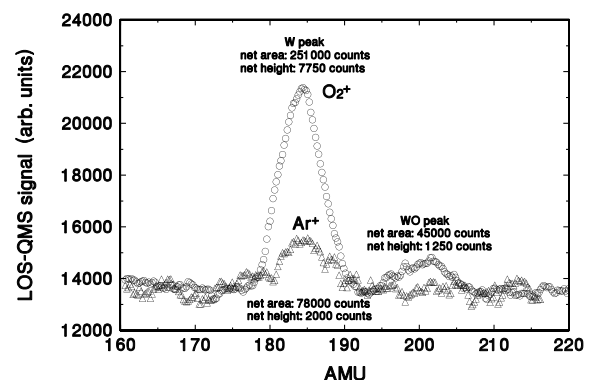


Fig. 3. LOS-QMS signal, averaged over eight mass scans, for W at 300 K, during bombardment by 10 keV  $O_2^+$  (5 keV/ $O^+$ ) or 10 keV  $Ar^+$ .

detect other atoms and molecules during  $O_2^+$  bombardment, such as C,  $CH_x$ , O,  $OH_x$ , CO,  $O_2$  and  $CO_2$ . No such particles were detected, indicating that the yields were below the noise level in the detection system.

During data collection, the mass was repeatedly scanned from about 160–220 amu while bombarding the W specimen with  $O_2^+$  ions. Typically, eight mass scans were averaged together in order to improve the signal-to-noise ratio. The large peak has been identified as W (masses 182, 183, 184 and 186 making roughly equal contributions, convolved into one peak by the system resolution) and the secondary peak as WO. In most of the data the WO peak can be observed but it is difficult to quantify because of the large background noise; efforts are underway to improve the signal-to-noise ratio so as to make use of the WO peak height data. In the following discussion only the W peak height is used.

Fig. 3 shows LOS-QMS spectra collected during bombardment by 10 keV  $Ar^+$  at a flux of about  $2 \times 10^{19}/m^2 s$ , and by 10 keV  $O_2^+$  (5 keV/ $O^+$ ) at a similar flux. Bombarding the W foil with  $Ar^+$  ions removed all surface oxygen within a few seconds, resulting in a spectrum with a W peak but no WO peak. The LOS-QMS signal at mass 184 obtained during bombardment with  $O_2^+$  is nearly four times larger than that detected with  $Ar^+$ . Since the particle fluxes are similar, but the  $Ar^+$  sputtering yield (from TRIM 2000 calculations and from mass-loss measurements; see Section 3.1) is 3.4 times larger than that of  $O^+$ , it appears that the LOS-QMS is primarily measuring erosion products that are not due to physical sputtering. It is reasonable to expect that slower moving chemically sputtered particles would have a higher probability of being ionised in the QMS ionizer, and transmitted through the QMS optics, than the more energetic physically sputtered particles. During bombardment with  $Ar^+$  there should be no chemical sputtering, so in this case the LOS-QMS yield (net W peak height of 2000 counts) can be attributed to purely physical sputtering. Then the component of the W peak obtained during  $O_2^+$  bombardment which could be attributed to physical sputtering should be approximately  $2000/3.4 = 590$  counts, or about 7.6% of the net peak height observed (7750 counts). Hence, the LOS-QMS signal at mass 184 must be dominated by particles released from the surface by a mechanism other than physical sputtering of pure W. Due to the relatively long ( $\sim 10$  s) response time of the QMS detection system, it was not possible to study the time delay behaviour of the emitted particles by turning the ion beam on and off.

Fig. 4 shows the W peak yield (net peak height divided by the  $O^+$  flux) from LOS-QMS during bombardment of W by  $O_2^+$  at 300 K, as a function of the oxygen energy (keV/ $O^+$ ). Since the data appear to indicate a threshold energy, they were fitted to an equation following the form of the revised Bohdanský equation [11] for sputtering (solid line). The fit is rea-

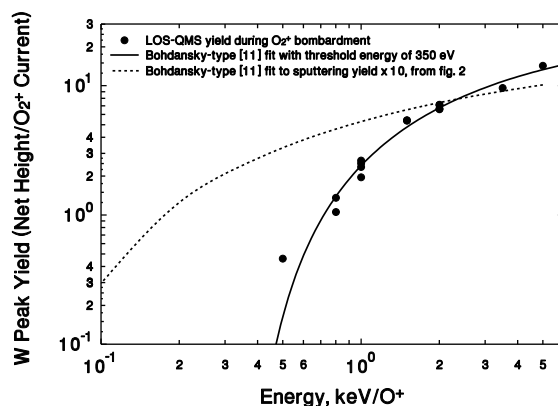


Fig. 4. LOS-QMS W peak yield (net W peak height divided by  $O_2^+$  beam current; arbitrary units) as a function of energy per  $O^+$  particle. The solid line is a least-squares fit to the data, using a Bohdanský-type [11] equation. The dashed line is the Bohdanský-type [11] curve for physical sputtering from Fig. 2, scaled up for comparison purposes.

sonably good, indicating a threshold energy of 350 eV/ $O^+$ , below which the W peak height is lost in the noise ( $\pm 500$  counts). The dashed line shows the Bohdanský fit to the physical sputtering yield (from Fig. 2), scaled up by a factor of 10 for comparison purposes. The threshold energy of 350 eV for the ‘chemical erosion’ detected by the LOS-QMS is much larger than the threshold energy of 44.5 eV for physical sputtering of pure W [5], indicating that the ‘chemical erosion’ processes and release mechanisms require the incident ions to have enough energy to break several bonds between surface atoms, or possibly even create displacements.

#### 3.4. Dependence of the LOS-QMS W peak yield on the $O_2^+$ ion flux

The LOS-QMS yield data at mass 184 (obtained with 2 keV/ $O^+$  on W at 300 K) are plotted as a function of the  $O_2^+$  current (proportional to the flux) in Fig. 5, along with a linear least-squares fit to indicate the trend. (2 keV/ $O^+$  was selected because it was the lowest energy for which the LOS-QMS yield was well above the noise level.) The yield decreased with increasing  $O_2^+$  current. Similar results were obtained at 1000 K. If, as discussed above at the end of Section 3.1, oxygen is being removed from the surface by some means such as diffusion or volatilization, the surface coverage of oxygen should increase with increasing  $O_2^+$  flux. Then the trend of decreasing yield with increasing current implies a dependence of the ‘chemical erosion’ rate on the surface coverage of oxygen; at higher oxygen coverage, the apparent ‘chemical erosion’ yield, as indicated by the W peak height, may be reduced by a change in the molecular weight of the sputtered particles, i.e., the size of

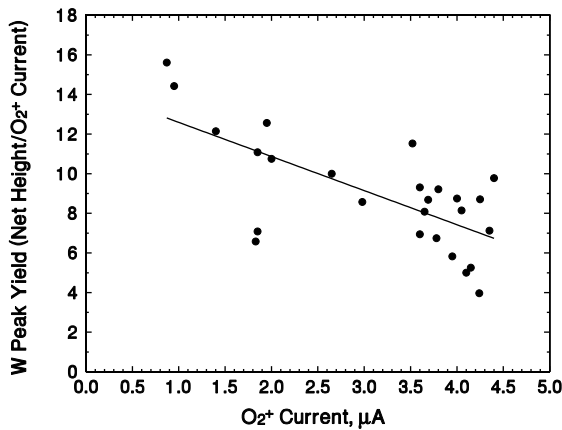


Fig. 5. LOS-QMS W peak yield as a function of  $O_2+$  beam current (arbitrary units) for  $2 \text{ keV}/O^+$  impact on W at 300 K. Solid line is a least-squares linear fit to the data.

$W_xO_y$  molecules may be increasing, but our LOS-QMS only detects up to  $WO_2$ .

### 3.5. Specimen temperature effects on LOS-QMS W peak yield

LOS-QMS signals were measured at temperatures from 300 to 1900 K, during bombardment with  $2 \text{ keV}/O^+$ . Only the mass 184 (W) peak was clearly visible at all temperatures. The W yield is plotted against specimen temperature in Fig. 6. It can be seen that there is a generally decreasing trend of the W peak with increasing temperature. The extensive scatter may be attributed to varying surface chemistry due to relatively

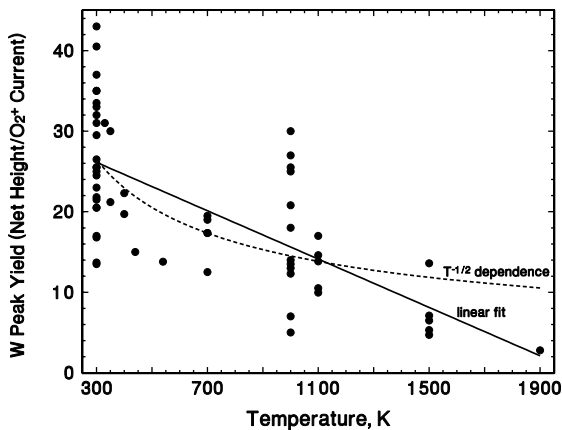


Fig. 6. LOS-QMS W peak yield as a function of W temperature (arbitrary units), during bombardment by  $4 \text{ keV } O_2+$  ( $2 \text{ keV}/O^+$ ). The solid line is a least-squares linear fit to the data, and the dashed line is a fit to a  $T^{-1/2}$  dependence.

small changes in surface composition. The solid line in Fig. 6 is a linear fit, and the dashed line is proportional to  $(T)^{-1/2}$ , where  $T$  is the temperature of the W specimen. A  $(T)^{-1/2}$  trend would be consistent with decreasing sensitivity of the QMS due to increasing particle velocity with increasing specimen temperature. This trend would result from a lower efficiency of ionization of the relatively higher velocity particles due to the shorter times taken to travel through the QMS ionizer. A stronger decrease with increasing temperature would indicate that the rate of ‘chemical erosion’ is decreasing, possibly due to alternate reactions such as  $O_2$  recombination and release (although we did not observe any increase in the  $O_2$  signal), or release of heavier  $W_xO_y$  molecules. It appears that the trend is stronger than  $(T)^{-1/2}$ .

### 3.6. Erosion of W due to simultaneous impact by $O_2+$ and $D_3+$ using LOS-QMS

W specimens were bombarded with  $4 \text{ keV}/O_2+$  ( $2 \text{ keV}/O^+$ ) and  $3 \text{ keV } D_3+$  ( $1 \text{ keV}/D^+$ ) simultaneously at 300 K. (As above,  $2 \text{ keV}/O^+$  was used because it was the lowest energy for which the LOS-QMS yield was well above the noise level;  $1 \text{ keV}/D^+$  was the lowest energy for which the  $D^+$  flux was large enough to obtain the desired flux ratios.) The simultaneous bombardment caused the LOS-QMS yield to drop to about 50% of the  $O^+$ -only yield, at both the W and WO peaks, when the flux ratio was 0.11  $O^+/D^+$  ( $1.2 \times 10^{20} D^+/m^2 s$ , and  $1.3 \times 10^{19} O^+/m^2 s$ ). Similar effects were observed at 500–1000 K. While in most experiments with flux ratios of  $O^+/D^+$  ranging from 11% to 24% the reduction was in the range of 30–50%, in one case the W peak signal was completely eliminated by the addition of the  $D^+$ , and in a few other cases the reduction in the yield was barely detectable. The observed variation in the yield reduction may be due to the same variations in surface chemistry that caused the scatter in the W yields in Figs. 5 and 6, and possibly also to variations in the overlap efficiency of the two ion beams. Due to the large scatter it was not possible to determine the dependence of the yield reduction on the  $O^+/D^+$  flux ratio.

The results indicate that the effect of simultaneous incidence of  $1 \text{ keV}/D^+$  is either to reduce the chemical component of the  $O^+$  sputtering of W, or to change the species emitted by ‘chemical erosion’, reducing the sizes of the W (mass 184) and WO (mass 200) peaks. The presence of large amounts of D in the near-surface might lead to the release of larger oxide molecules, such as  $W_2O_5$ , which would have different cracking patterns in the QMS ionizer. Molecular dynamics calculations by Landman and Wuerz [15] suggest that the deuterium destroys  $WO_2$  molecules and removes oxygen by sputtering.

#### 4. Conclusions

It is evident from comparing mass-loss and LOS-QMS measurements that when tungsten is bombarded by 0.2–10 keV  $O_2^+$  (0.1–5 keV/ $O^+$ ), its rate of erosion is primarily determined by physical sputtering. LOS-QMS data indicate a ‘chemical erosion’ component, which is measurable due to the significantly higher sensitivity of the LOS-QMS technique to chemically sputtered particles with near thermal energy, as compared to the relatively higher energy physically sputtered particles. The erosion results obtained by the mass-loss technique, bombarding with both  $O_2^+$  and  $D_3^+$ , do not support the hypothesis that the presence of the oxygen reduces the effective surface binding energy of W, leading to significantly enhanced erosion by  $D^+$ , for the energies used in this study.

The  $O^+$ -induced ‘chemical erosion’ process is complex, with an apparent threshold energy of 350 eV/ $O^+$ , well above the threshold energy for physical sputtering, 44.5 eV. This may indicate that the ‘chemical erosion’ process requires that several bonds be broken by the ion. The LOS-QMS yield at mass 184 (W) decreases with increasing temperature and  $O_2^+$  flux. The effect of adding  $D^+$  to  $O^+$  incident on W at temperatures of 300–1500 K is to reduce the LOS-QMS signal for the W peak. This indicates that the addition of  $D^+$  either reduces the ‘chemical erosion’ of W by  $O^+$ , or changes the distribution of species emitted from the surface, with the possibility that heavier oxide species go undetected.

The scatter in both the mass-loss measurements of the physical sputtering yields and the LOS-QMS measurements of the ‘chemical sputtering’ yields is taken to indicate that the composition of the surface, in terms of the content of oxygen and other impurities, can significantly change the measured yields.

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