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# Effect of purity on the vacancy defects induced in self-irradiated tungsten: a combination of PAS and TEM

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## Abstract:

Vacancy defects in tungsten induced by self-irradiation were characterized by positron annihilation spectroscopy (PAS) and transmission electron microscopy (TEM). Taking advantage of their complementarity, defects ranging from single vacancies up to vacancy clusters were detected, and the effects of sample purity (99.95 wt.% and 99.9999 wt.%) on their formation and evolution under low damage dose (0.01 to 0.02 dpa) irradiation with 20 and 1.2 MeV-W ions were studied at room temperature (RT), 500 and 700 °C respectively. When irradiation was performed at RT, PAS probed mainly single vacancies. At high irradiation temperatures, larger vacancy clusters were detected by both techniques. Both PAS and TEM revealed larger vacancy clusters in the purest samples after irradiation at 500 and 700 °C. A significant difference in the evolution of vacancy-type defects related to sample purity was observed. In view of the properties (migration, trapping) of some light-element impurities (LEs), present at high concentrations, determined by first-principles calculation, it is reasonable to assign the effect of purity during the irradiation response to the formation of vacancy-impurity complexes, which is critical for the understanding of the behavior of tungsten in the future fusion reactor.

## 1. Introduction

Tungsten, the basic material for several components facing the thermonuclear fusion plasma in the ITER (International Thermonuclear Experimental Reactor) experimental tokamak, in particular for the

28 divertor [1,2], is also envisaged to cover the first wall of DEMO (DEMONstration Power Plant) [3]. Its  
29 high melting point, efficient thermal conductivity, and low sputtering yield are advantageous for the  
30 secure operation of future fusion reactors in which materials will be subjected to extreme conditions.  
31 Tungsten will have to undergo high heat fluxes and the impact of hydrogen isotopes and helium  
32 (respectively the plasma fuel and the fusion reaction product). According to theoretical and  
33 experimental work, these severe conditions induce the formation of bubbles [4] leading to a fuzzy [5]  
34 and blistering surface [6] as well-known consequences of helium and hydrogen introduction,  
35 respectively. Simultaneously, high-energy particles (14.1 MeV neutrons and 3.5 MeV  $\alpha$ ) bombard the  
36 plasma-facing walls, creating various defects whose evolution is probably accelerated by the high  
37 temperature, and giving rise to drastic modifications in the tungsten microstructure. Irradiation-  
38 induced defects such as dislocation loops [7,8] and vacancy-type defects [9,10] have been  
39 experimentally observed in tungsten using either TEM or PAS. Only a few studies report analysis of  
40 neutron irradiated tungsten using PAS [11–14]. Furthermore, a large number of studies [15–17] have  
41 demonstrated that the transmutation elements (TEs) interact strongly with the aforementioned  
42 irradiation-induced defects. Their precipitation results in further degradation of mechanical properties  
43 [18–20]. As all these irradiation-induced defects negatively affect the performance and reliability of  
44 future reactors, it is critical to understand their nature, formation and evolution mechanisms to better  
45 predict them and potentially mitigate them.

46 Recently, Castin et al. [21] demonstrated the influence of carbon on the formation of loops by using  
47 object kinetic Monte Carlo (OKMC) modeling and secondary ion mass spectroscopy (SIMS). Besides,  
48 first-principle calculations predicted that vacancy-type defects interact strongly with LEs. Table 1 sums  
49 up the results of first-principles calculations of the LE (H, C, N, O) properties [22–30], indicating that LE  
50 (H, C, N, O) are apt to locate at octahedral or tetrahedral interstitial sites in the vicinity of single  
51 vacancies in the tungsten matrix. By comparing the migration energy of the single vacancies ( $E_m^{V_1} =$   
52  $1.66\text{ eV}$  [31]), the lower migration energies  $E_m^{X_1}$  of single LE atoms indicates their higher mobility in  
53 the tungsten matrix than that of single vacancies. In addition, the strong binding energies between LE

54 atoms and single vacancies indicate that LEs tend to be trapped at single vacancies. It is possible to  
55 trap more than one LE atom in a single vacancy. For instance, a single vacancy can trap as many as 12  
56 hydrogen atoms [22], 4 carbon atoms [23], 6 nitrogen atoms [24], and 6 oxygen atoms [25]. However,  
57 except for these theoretical results, it is difficult to find an experimental study concerning LE-vacancy  
58 complexes and their impact on the evolution of the microstructure of tungsten under irradiation. In a  
59 similar study on carbon-doped bcc iron, Vehanen et al. [32] demonstrated the practicability of positron  
60 annihilation spectroscopy and showed that carbon-vacancy complexes are formed in stage III (200 K,  
61 related to V migration) due to the trapping of vacancies by carbon atoms, impeding the clustering of  
62 vacancies up to about 450 K when dissociation of the V-C complex was observed. They also showed  
63 that at about 350 K carbon atoms become mobile, and can be trapped at V-C complexes. The greater  
64 the number of carbon atoms  $n$ , the more the V-C <sub>$n$</sub>  complexes generated hinder the trapping of  
65 positrons.

$X$	$E_f^X$ (eV)	$E_m^X$ (eV)	$E_b^{V_1-X_1}$ (eV)	$E_b^{V_1-X_n}$ (eV)
<b>H</b>	4.05 (SS)	0.21 (TIS-TIS) [27]	1.24 [28]	0.20 [22]
	0.93 (TIS) [26]	0.59 (OIS-TIS)		(V <sub>1</sub> -H <sub>12</sub> )
	1.27 (OIS)			
<b>C</b>	4.25 (SS)	1.46 (TIS-OIS) [23]	1.93 [23]	0.55 [23]
	2.24 – 2.28 (TIS) [28]	3.87 (OIS-TIS)		(V <sub>1</sub> -C <sub>4</sub> )
	0.78 (OIS)			
<b>N</b>	-0.13 (SS)	0.73 (TIS-OIS) [29]	2.48 [24]	9.66 [24]
	-3.06 (TIS) [29]	3.60 (OIS-TIS)		(V <sub>1</sub> -N <sub>6</sub> )
	-3.79 (OIS)			
<b>O</b>	0.5 (SS)	0.17 (TIS-TIS)[25]	3.05 [25]	11.21 [24]
	-1.75 (TIS) [25]	0.32 (TIS-OIS)		(V <sub>1</sub> -O <sub>6</sub> )
	-1.43 (OIS)			

66 *Table 1: Calculated formation energy  $E_f^X$ , migration energy  $E_m^X$  of element  $X$  and its binding energy with a*  
67 *tungsten single vacancy  $E_b^{V_1-X_1}$ , and the binding energy,  $E_b^{V_1-X_n}$  of a tungsten single vacancy with the maximum*  
68 *of LE atoms that can be trapped,  $n$ . (SS: substitutional site TIS: tetrahedral interstitial site, OIS: octahedral*  
69 *interstitial site) [19–27].*

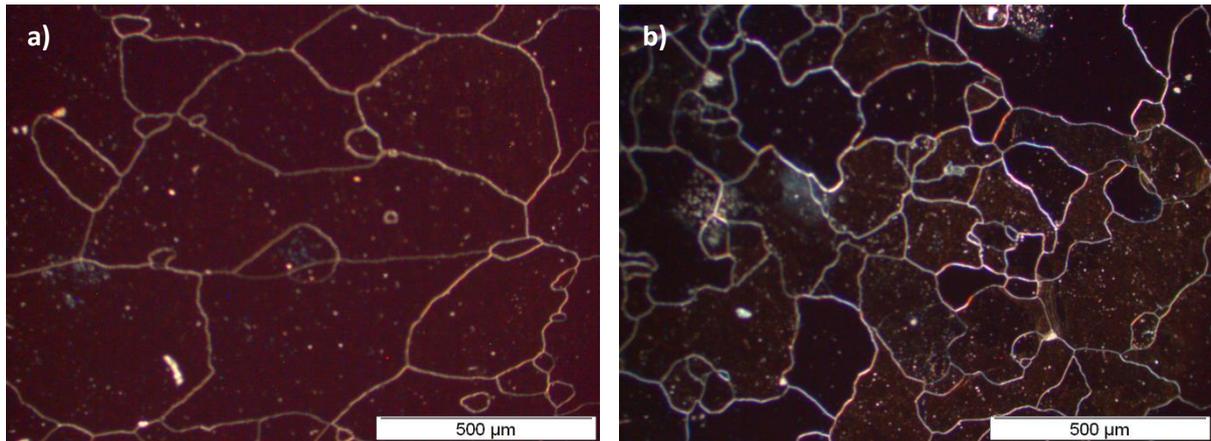
70 In this paper, we show the first experimental results elucidating the impact of LE-vacancy interactions  
71 on the vacancy's evolution in irradiated tungsten. We introduced vacancy-type defects into tungsten  
72 samples of two purity levels i.e. 3N-HP (99.95 wt.%) and 6N-XHP (99.9999 wt.%) by self-irradiation of

73 20 and 1.2 MeV at various temperatures (RT, 500 °C, and 700 °C). Post-irradiation characterizations  
74 were performed by TEM to directly observe the cavities with sizes above ~0.5 nm. To characterize the  
75 vacancy-type defects below the TEM detection limit, we employed PAS as it enables the probing of  
76 vacancy-type defects from single vacancies to vacancy clusters made of up to around 30 vacancies.

## 77 **2. Experimental details**

### 78 **2.1 Sample preparation and irradiation conditions**

79 This experimental study was carried out in polycrystalline W samples with two purity levels. The lower  
80 purity samples were laminated high purity (HP) samples (99.95 wt.%, 3N-HP, H: <910 ppm C: <460 ppm  
81 N: <130 ppm O: <345 ppm) purchased from Goodfellow. The extra-high purity samples (XHP) were  
82 provided by Forschungszentrum Jülich (99.9999 wt.%, 6N-XHP, H, C, O, and N undetectable by LA-ICP-  
83 MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry)). Two shapes of samples, adapted  
84 to the characterization technique, were used: 7 × 7 mm<sup>2</sup> squares for PAS and Ø3 mm discs for TEM.  
85 They were first polished using abrasive SiC papers (P600 to P2500) and then the surface was improved  
86 by flocked felt (FD3 to FD1) from the ESCIL company. Next, the single-face mirror-polished samples  
87 were rinsed in an ultrasonic bath for 20 minutes in acetone and then in ethanol. Then, as-polished  
88 samples were annealed in a high vacuum (< 10<sup>-7</sup> mbar) furnace at 1700 °C for 3 hours to eliminate the  
89 native and polishing-induced defects. The grain sizes after annealing were evaluated by light  
90 microscopy (Figure 1). The mean size was about 500 µm and 200 µm for the 3N-HP sample and 6N-  
91 XHP sample, respectively. The as-annealed discs (Ø3 mm) prepared for TEM observations were  
92 electropolished into thin foils (electron transparent areas of ~60 nm thickness) using Tenupol-5 with a  
93 double jet of prepared NaOH solution (0.05 mol/L, 15 °C, and 15 V) for 10 minutes. Lastly, the thick  
94 square samples (thickness > 100 µm) were checked prior to irradiation by PAS for further comparison,  
95 and the thin foil samples were qualified by TEM. The qualified thin foil samples have homogenous large  
96 grains with the lowest possible dislocation density and other microstructural defects.



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98

*Figure 1: Well-annealed polycrystalline tungsten samples a) 3N-HP 99.99 wt.% and b) 6N-XHP 99.9999 wt.%*

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Self-irradiation was performed at various temperatures RT, 500, and 700 °C, and the energy of the

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tungsten ions was adapted to the depth of the region that could be probed by TEM and PAS. The thick

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square samples were ex-situ irradiated by 20 MeV-W<sup>+</sup> and the thin foils were in situ damaged with 1.2

102

MeV-W<sup>+</sup> in the electronic transmission microscope at the JANNuS (Joint Accelerators for Nano-science

103

and Nuclear Simulation) platform [33]. The ion beam incidence was fixed at 15° for the most energetic

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ions and 45° for in situ irradiations. The profiles of induced damage dose versus depth were estimated

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using the quick calculation option based on Kinchin-Pease formalism in the SRIM-2008 (The Stopping

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and Range of Ions in Matter) program. The value of the displacement energy threshold  $E_d$  was fixed at

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55.3 eV as recommended by Dudarev [34] and the lattice binding energy  $E_b$  was 0 eV[35]. As shown in

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Figure 2, for pertinent fluences ( $7.48 \times 10^{12} \text{ cm}^{-2}$  for 20 MeV-W<sup>+</sup> in thick samples and  $1.8 \times 10^{12} \text{ cm}^{-2}$  for

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1.2 MeV-W<sup>+</sup> in lamella samples), the mean damage dose in the characterized region (the first 700 nm

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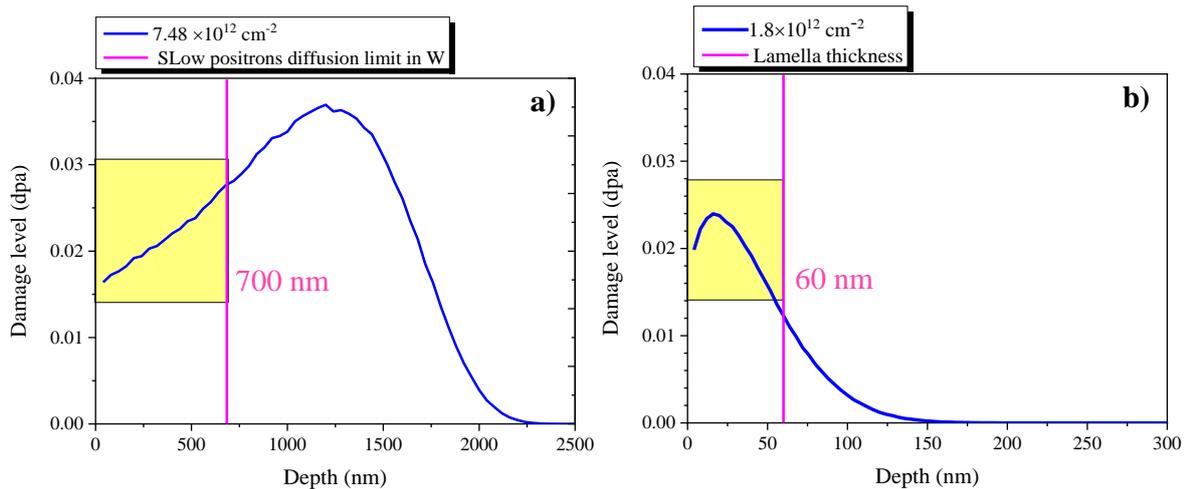
and 50 nm for PAS and TEM, respectively) was equivalent for both energy irradiations, around 0.02

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dpa. The experimental fluxes were fixed at  $2.8 \times 10^{10} \text{ cm}^{-2} \cdot \text{s}^{-1}$  and  $3.3 \times 10^9 \text{ cm}^{-2} \cdot \text{s}^{-1}$ , respectively, in

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order to obtain a comparable mean damage rate of about  $5 \times 10^{-5} \text{ dpa} \cdot \text{s}^{-1}$ .



113

114 *Figure 2 : a) Damage profile of self-irradiation with  $7.48 \times 10^{12} \text{ W}^+ \cdot \text{cm}^{-2}$  (15 °, 20 MeV), b) damage profile of self-*  
 115 *irradiation with  $1.8 \times 10^{12} \text{ W}^+ \cdot \text{cm}^{-2}$  (45°, 1.2 MeV) according to SRIM2008 with Kinchin-Pease formalism. The*  
 116 *characterized region depends on the thickness that can be probed by slow positrons: at most 700 nm for 25*  
 117 *keV [36] for PAS measured samples and about 60 nm for TEM observed samples.*

## 118 2.2 Characterization methods

### 119 2.2.1 Positron annihilation spectroscopy (PAS)

120 PAS takes advantage of two fundamental properties of positrons. First, they annihilate with electrons  
 121 of the solids, making it possible to probe the electronic structure of materials. Second, they can be  
 122 trapped in open volumes such as vacancy-type defects (single vacancies, vacancy clusters,  
 123 dislocation...), and then annihilate with surrounding electrons, enabling the detection of the nature  
 124 and concentration of the defects. In the present work, a slow positron beam was coupled to a Doppler  
 125 Broadening spectrometer (SPB-DB) developed at CEMHTI (Conditions Extrêmes et Matériaux: Haute  
 126 Température et Irradiation). This device exhibits high efficiency in the characterization of tiny vacancy-  
 127 type defects in the first micron under the surface of solid samples (see [37] for further technical details).  
 128 In the SPB-DB experiment, a monoenergetic positron beam produced by a 22-sodium source is guided  
 129 onto the sample, where it appears as a 2-3 mm spot. At the same time, it is accelerated with adjustable  
 130 energy ranging from 0.5 to 25 keV which allows an effective probing of vacancy-type defects within  
 131 increasing depth. For the energy ranges from 0.5 to 25 keV, the slow positrons probe until 700 nm in  
 132 tungsten. The implantation profile of monoenergetic positrons is a Makhovian type [36]. When the

133 positrons have lost their kinetic energy, the thermalized positrons diffuse in the material and end up  
134 by annihilating with electrons, emitting in most cases two  $\gamma$ -rays with an energy of  $511 \pm \Delta E_\gamma$  keV. The  
135 energy deviation  $\Delta E_\gamma$  is proportional to the longitudinal kinetic momentum of the  $e^+e^-$  pairs just before  
136 the annihilation and causes Doppler Broadening (DB) of the annihilation line. The DB spectrum is the  
137 photon count number as a function of their energy, i.e. the  $e^+e^-$  pairs' kinetic momentum, and is also  
138 called the  $e^+e^-$  annihilated pairs momentum distribution. Its shape depends on the positron states  
139 where it annihilates, i.e. either it is delocalized in the lattice or trapped at a vacancy-type defect. When  
140 a positron is trapped at a vacancy-type defect, the probability of it annihilating with core electrons or  
141 high momentum electrons is decreased compared to the case where it is delocalized in the lattice. The  
142 measured DB spectrum of material with vacancy-type defects is, therefore, thinner than that of a  
143 defect-free one. Two line-shape parameters  $S$  and  $W$  were used to quantify the evolution of the DB  
144 spectrum.  $S$  and  $W$  were respectively the low and high momentum annihilation fractions. They were  
145 equal to the ratio of photon counts in the central region close to 511keV and in the two wing regions  
146 respectively of the DB spectrum over the total counts of the full spectrum.  $S$  is related to the positron  
147 annihilations with mostly valence electrons.  $W$  is associated with annihilation which occurs mainly  
148 between positrons and core electrons. In this study, the momentum ranges chosen for the calculation  
149 of  $S$  and  $W$  were  $0 - |2.64| \times 10^{-3} m_0c$  and  $(|9.80| - |24.88|) \times 10^{-3} m_0c$  ( $m_0$ : electron mass,  $c$ : light speed).  
150 Since the surrounding electrons of positrons trapped in open volumes are mainly valence electrons  
151 with low momentum, the annihilation that occurs at vacancy-type defects leads to an increase in  $S$  and  
152 a decrease in  $W$ , in contrast to the annihilation taking place in the delocalized perfect lattice. It is crucial  
153 to point out that each annihilation state can be brought out with specific values of  $S$  and  $W$  in each  
154 material: that is why the curve  $S(W)$  exhibits the nature of the principal annihilation states. Regarding  
155 tungsten, as shown in Figure 3, the specific values for a perfect lattice ( $S_L = 0.367(4)$ ,  $W_L = 0.084(5)$ ) and  
156 single vacancies ( $S_{V1} = 0.417(1)$ ,  $W_{V1} = 0.057(1)$ ) were determined in previous work [38,39], as well as  
157 those of vacancy-clusters ( $S_{VN} = 0.503(1)$ ,  $W_{VN} = 0.036(1)$ ) [39] which concerns probably the largest  
158 clusters detectable in our SPB-DB experiments performed in tungsten. The  $S_{VN}$ ,  $W_{VN}$  values were

159 measured in W irradiated with 20 MeV-W ions with a fluence of  $3.7 \times 10^{14} \text{ W}^+ \cdot \text{cm}^{-2}$  (1dpa) and post-  
 160 annealed at 550 °C/1h. It can be shown that the annihilation characteristics no longer change when  
 161 the number of vacancies in the cluster increases above a threshold. It has been found from positron  
 162 lifetime calculations [40] that this threshold is approximately 20 to 30 in tungsten. The diameter of a  
 163 cluster of 27 monovacancies in W was evaluated to be 0.94 nm for  $N = 27$  if no relaxation occurs [41].  
 164 This suggests that the  $S_{Vn}$ ,  $W_{Vn}$  values could correspond to annihilation at such vacancy clusters made  
 165 of at least 20-30 vacancies i.e. a diameter of approximately 1 nm. Moreover, it has been demonstrated  
 166 that, in the  $S(W)$  graph, the absolute value of the slope of the segment lines  $R(= \left| \frac{S_{Vn}-S_L}{W_{Vn}-W_L} \right|)$  linking  
 167 the lattice point  $(S_L, W_L)$  to that of the defect  $V_n (S_{Vn}, W_{Vn})$ , where  $n$  is the number of vacancies in the  
 168 vacancy cluster ( $n = 1, 2, 3..$ ), increases with  $n$  or the size of vacancy clusters. The  $(S, W)$  points located  
 169 at the same line going through the lattice point indicate that only one defect or the same size defect  
 170 distribution with various global concentration is detected. For instance, in Figure 3, the line  $L_1$  indicates  
 171 annihilation at single vacancies and the line  $L_2$  indicates vacancy clusters. If we assume that the  
 172 annihilation rate is 100 % (in the lattice or the defect), it is clear that, at the same line, the closer the  
 173  $(S, W)$  point is to the defect characteristic point  $(S_{Vn}, W_{Vn})$ , the higher the concentration is.

174 **In the SPB-DB measurement, the DB spectrum is recorded as a function of positron energy E. One high**  
 175 **purity germanium detector with about 10 % dead time offers a high resolution (< 1.3 keV at 511 keV)**  
 176 **and detection efficiency (> 25 % at 1.33 MeV) of the  $\gamma$ -rays.** To obtain valid statistics, at least  $4 \times 10^5$   
 177 counts are cumulated for each positron energy in the Doppler peak –in the region of momentum  
 178 between  $-24.88$  to  $+24.88 \times 10^{-3} m_0 c$ - and  $S, W$  values are extracted from each spectrum. In addition to  
 179 the  $S(W)$  plot, the curves  $S$  and  $W$  as a function of positron energy  $E$ ,  $S(E)$ , and  $W(E)$  respectively,  
 180 illustrate the depth distribution of the vacancy-type defects. Furthermore, using the VEPTFIT program  
 181 [42] the  $S W$  depth profiles can be extracted from the  $S(E)$  and  $W(E)$  curves by fitting the experimental  
 182 data. The program calculates the  $S(E)$  and  $W(E)$  by taking into account the implantation profiles and  
 183 diffusion of positrons using a model that considers the solids as a sequence of several homogenous

184 layers with independent  $S$  and  $W$  annihilation characteristics, thickness, and positron effective  
 185 diffusion length  $L_{eff}^+$  for each layer. Note that the diffusion of positrons is limited by their trapping at  
 186 defects. Hence, the effective diffusion length  $L_{eff}^+$  can be written as follows [43]:

$$L_{eff}^+ = \sqrt{\frac{D^+}{\lambda_L + \sum_{i=1}^n K_{d_i}}} \quad (1)$$

187 where  $K_{d_i}$  are the positron trapping rates at various detected defects  $i$  (single vacancy, vacancy clusters  
 188  $V_N$ , dislocations, etc.),  $D^+$  is the intrinsic positron diffusion coefficient ( $D^+ = 1.26 \times 10^{-4} \text{ m}^2 \cdot \text{s}^{-1}$  for  
 189 tungsten [44]) and  $\lambda_L$  the lattice annihilation rate ( $\lambda_L = 1/\tau_L$ ,  $\tau_L = 101 - 105 \text{ ps}$  [45]). The trapping rate  $K_d$   
 190 at the detected defects  $d$  is the product of their concentration  $C_d$  and their specific trapping coefficient  
 191  $\mu_d$ . The trapping coefficient of single vacancies in tungsten is approximated to the value determined  
 192 for the single vacancy in tantalum which presents a similar atomic number ( $Z = 73$ ) ( $\mu_V = 6 \pm 3 \times 10^{-15}$   
 193  $\text{m}^3 \cdot \text{s}^{-1}$  [46]). It is expected that the specific trapping coefficient for vacancy clusters  $V_N$  is about  $1.6 \times$   
 194  $10^{-13} \text{m}^3 \cdot \text{s}^{-1}$  as it can be extrapolated from TEM and PAS measurements in aluminum [46]. It should be  
 195 mentioned that data acquired at low energy below 2 keV are disregarded in the fittings because the  
 196 model used in the VEPFIT program poorly describes the positron properties for such low energies.

## 197 2.2.2 Transmission Electron Microscopy (TEM)

198 To complement PAS characterization, TEM observations of the 3N-HP and 6N-XHP samples irradiated  
 199 with 1.2 MeV-W ions were performed on two instruments. A JEOL ARM200F field emission gun  
 200 microscope operating at 200 kV and equipped with double spherical aberration correctors was used  
 201 for samples irradiated at 500 °C. The thin lamellae irradiated at 700 °C were observed with a Philips  
 202 CM20 also operating at 200 kV. Defocus series were recorded from a focus of  $-0.4 \mu\text{m}$  to  $+0.4 \mu\text{m}$ .  
 203 According to the microscope performance, the Fresnel contrast method was able to characterize the  
 204 cavities with a diameter above 0.5 nm. Since both the out-of-focus level and the magnification impact  
 205 on the apparent size of cavities [47], all TEM observations were carried out in comparable conditions,  
 206 i.e. acceleration voltage and magnification. The sizing of cavities was performed on over-focused

207 images with the same defocus (+250 or +300 nm), to minimize the uncertainty on the size  
208 determination.

209 The thickness of the thin region where cavities were characterized was measured using EFTEM (Energy  
210 Filtered Transmission Electron Microscopy) for the 500 °C irradiated samples. The thickness of the 6N-  
211 XHP lamella varied from 70 to 110 nm in the observed region, so we used an average value of  $90 \pm 30$   
212 nm to estimate the cavities' density. For the 3N-HP thin lamella, the thickness of the observed region  
213 was quite constant at about  $55 \pm 20$  nm. For the 700 °C irradiated samples, the thickness could not be  
214 measured. It was estimated as the mean value of the thicknesses measured by EFTEM in several W  
215 thin lamellae prepared in the same conditions. The thickness was fixed at  $35 \pm 20$  and  $60 \pm 50$  nm for  
216 3N-HP and 6N-XHP samples respectively.

217 The uncertainty on the diameter  $d$  and the density  $D$  of cavities can be estimated by the following  
218 equations [48]:

$$\Delta d = d \times \left( \frac{\Delta N}{N} + \frac{\Delta d_{av}}{d_{av}} \right) \quad (2)$$

219 where  $\Delta d$  is the total uncertainty of the diameter  $d$ ,  $\frac{\Delta N}{N}$  the error on the number  $N$  of cavities which  
220 equals to  $\frac{1}{\sqrt{N}}$ , and  $\frac{\Delta d_{av}}{d_{av}}$  is the error on the diameter measurement which was experimentally estimated  
221 at 15 %. To determine the latter term, we chose 10 cavities of different sizes to estimate the minimum  
222 and maximum size for each cavity and finally, we found the average size and the standard deviation  
223 (for each cavity).  $\frac{\Delta d_{av}d}{d_{av}d}$  was taken as the average ratio of the standard deviation over the average size:

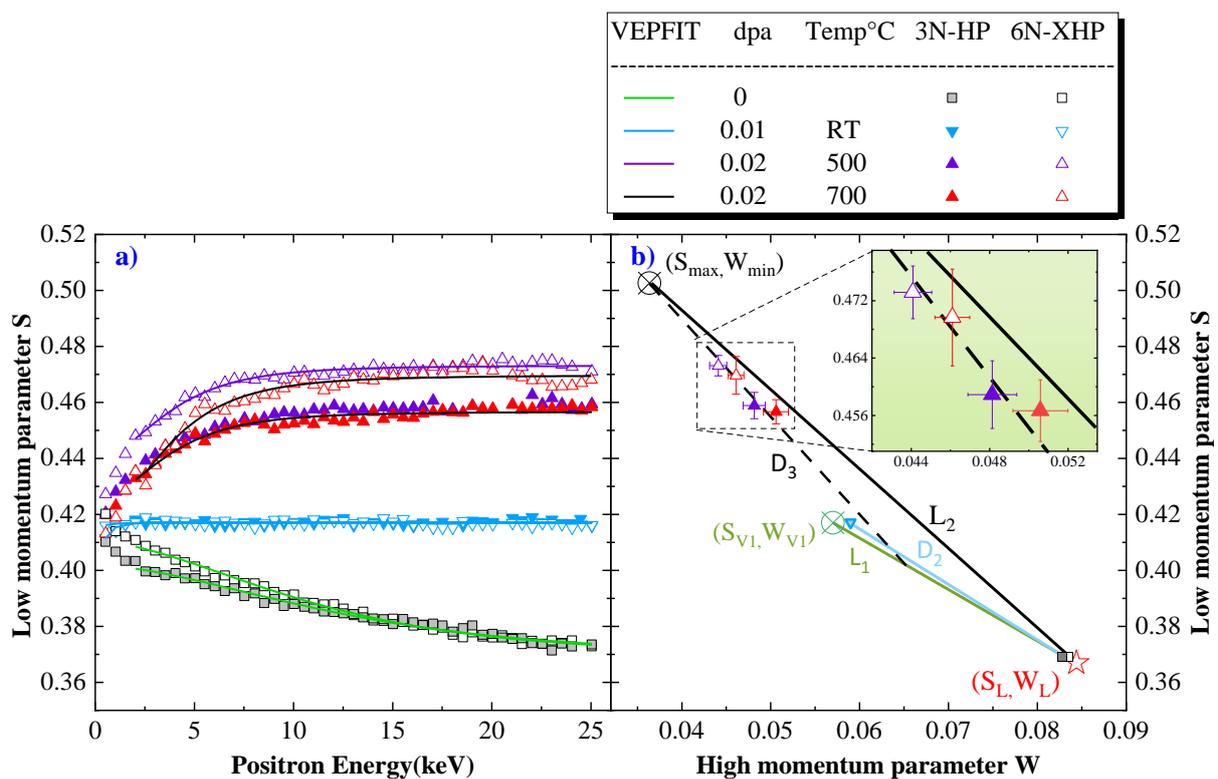
$$\Delta D = D \times \left( \frac{\Delta N}{N} + \frac{\Delta t}{t} \right) \quad (3)$$

224 where  $\Delta D$  is the total uncertainty of the density  $D$  and  $\frac{\Delta t}{t}$  is the error on the thickness  $t$  measurement  
225 equal to the ratio of uncertainty over measured thickness.

226 **3. Results**

227 **3.1 PAS results**

228 Figure 3 (a) shows the low momentum annihilation fraction  $S$  as a function of positron energy  $E$  in  
 229 tungsten samples of two purities, 3N-HP and 6N-XHP, before and after irradiation at various conditions  
 230 (room temperature (RT), 500 °C and 700 °C). It should be pointed out that the  $W(E)$  curves are the  
 231 reverse of the  $S(E)$  and consequently they are not shown in Figure 3. The results of the experimental  
 232 data adjustment i.e.  $S(E)$  and  $W(E)$  using the VEPFIT program are reported in Table 2. In Figure 2 (b),  
 233 the low momentum fraction  $S$  extracted from these fittings was plotted as a function of the high  
 234 momentum fraction  $W$  also extracted from these fittings. The error bars are not shown for the virgin  
 235 and RT irradiated samples because they are smaller than the size of the symbols.



236  
 237 *Figure 3: a: Low momentum annihilation fraction  $S$  as a function of positron energy and b: the fit extracted*  
 238 *values  $S$  as a function of the high momentum annihilation fraction  $W$  ones in 3N-HP  $W$  samples (solid symbols)*  
 239 *and 6N-XHP samples (open symbols), before irradiations (square ■(3N) □(6N)) after irradiation at room*  
 240 *temperature (0.01 dpa downward triangle ▼(3N) ▽(6N)), at high temperatures (upward triangle ▲(3N)*  
 241 *△(6N), plotted in purple for irradiation performed at 0.02 dpa, 500 °C, and in red for 0.02 dpa 700 °C)*

242 **For virgin W samples**, the slow decrease in  $S$  with increasing positron energy indicates that a  
 243 considerable fraction of positrons diffuse back to the surface. These experimental data of the two  
 244 virgin samples can be fitted with VEPFIT by using a single homogenous layer model. The  $S$  and  $W$   
 245 characteristics found in this layer are very similar for both types of materials 3N-HP and 6N-XHP (Table  
 246 2), and the effective diffusion length is long in both cases (3N-HP:  $L_{eff}^+ = 130\text{ nm}$ , 6N-XHP:  $L_{eff}^+ =$   
 247  $105\text{ nm}$ ) within the range reported in the literature (between 80 and 140 nm) [49] for intrinsic  
 248 diffusion in polycrystalline W with a purity of 99.95 %wt. Thus, the annihilation occurs both in the  
 249 perfect lattice and at the surface of the samples. In Figure 3 (b),  $SW$  values extracted for both virgin  
 250 materials using the VEPFIT program are close to the annihilation characteristics of the tungsten perfect  
 251 lattice. These results indicate that samples of both purities show similar positron annihilation  
 252 characteristics before irradiation and that the density of open volume defects is below the detection  
 253 limit of the SPB-DB (i.e. approximately  $10^{24}\text{ m}^{-3}$ ).

<b>Sample</b>	<b>Purity wt.%</b>	<b>Damage level(dpa)</b>	<b>Temperature °C</b>	<b>S</b>	<b>W</b>	<b><math>L_{eff}^+</math> (nm)</b>
G-35	99.95	0	-	0.3690(2)	0.0828(4)	132(6)
J-17	99.9999	0	-	0.3690(2)	0.0835(4)	105(4)
G-04	99.95	0.01	RT	0.4172(17)	0.0590(6)	0.6(1.7)
J-05	99.9999			0.4170(16)	0.0590(9)	0.4(0.2)
G-05	99.95	0.02	500	0.4589(21)	0.04814(9)	17(2)
J-11	99.9999			0.4723(38)	0.0431(8)	9(1)
J-06				0.4741(32)	0.0434(14)	11(2)
J-15				0.4726(37)	0.0442(10)	17(2)
G-02	99.95	0.02	700	0.4567(43)	0.0506(12)	14(2)
J-03	99.9999			0.4697(68)	0.0461(9)	17(2)

254 *Table 2: irradiation conditions of 3N-HP and 6N-XHP samples and the positron annihilation characteristics*  
 255 *obtained from the adjustment of  $S(E)$ ,  $W(E)$  experimental data measured in virgin and as-irradiated samples*  
 256 *using the VEPFIT program with one homogenous layer model.  $S$ ,  $W$ , and  $L_{eff}^+$  are the extracted values for the*  
 257 *damaged layer.*

258 **After irradiation (0.01 dpa) at RT**, quasi-identical positron annihilation characteristics were found in  
 259 3N-HP and 6N-XHP samples.  $S$  increases slightly and forms a plateau in a large part of the energy range,

260 indicating a homogenous distribution of induced defects in the region probed by positrons as is  
 261 expected from the SRIM calculations. This was confirmed by the data fitting which required only a  
 262 single layer to model the characterized region (0-700 nm). In Figure 3 (b), the  $S$  and  $W$  fitted values are  
 263 linked to the lattice point (star symbol) by a dotted line  $D_2$ . The absolute value of the  $D_2$  slope  $R$  slightly  
 264 exceeds that of the single vacancy line  $L_1$ , meaning that the induced defects are mostly related to small  
 265 vacancy clusters  $V_n$ , the majority of which are single vacancies. As shown in table 2, the estimated  
 266 effective diffusion length  $L_{eff}^+$  of positrons in the damaged region is extremely short ( $< 4$  nm) for both  
 267 tungsten purities, indicating a very high trapping rate of positrons  $K_D$  of about  $1.5 \pm 0.5 \times 10^{14} \text{ s}^{-1}$   
 268 estimated using equation (4) with an intrinsic diffusion  $L^+$  fixed at 135 nm [50] and a lattice positron  
 269 lifetime of 105 ps [40]. That could correspond to a maximum concentration of whole vacancy defects  
 270 of about  $10^{27} \text{ m}^{-3}$  (using a trapping coefficient of  $\mu_V = 6 \pm 3 \times 10^{-15} \text{ m}^{-3} \cdot \text{s}^{-1}$  [46]).

$$K_D = \lambda_L \left[ \left( \frac{L^+}{L_{eff}^+} \right)^2 - 1 \right] \quad (4)$$

271 **For irradiation (0.02 dpa) at high temperatures (500 °C and 700 °C)**, the  $S(E)$  curves exhibit a drastic  
 272 increase in  $S$  below 10 keV before reaching a plateau value. Note that for the same sample purity, the  
 273  $S$  plateau values (and  $W$  ones not shown here) are close for both high irradiation temperatures 500 °C  
 274 and 700 °C. For the same irradiation temperature, these plateau values depend strongly on the purity  
 275 of  $W$  samples, indicating a meaningful difference in induced defects between the two types of samples  
 276 3N-HP and 6N-XHP. The experimental data were adjusted using a single layer model (solid line in Figure  
 277 3 (a)) and the  $S$  and  $W$  values extracted for this damaged layer are reported in Table 2 and plotted in  
 278 Figure 3 (b). In this figure, it can be observed that the  $SW$  points measured for the irradiations  
 279 performed at high temperature are well above the single vacancy line  $L_1$ , clearly indicating that large  
 280 vacancy clusters were formed. Moreover, it was found that the  $SW$  points for the irradiation performed  
 281 at 500 and 700 °C are very close, even if, for irradiation at 700 °C, the data closer to the line  $L_2$  signifying  
 282 the largest detectable vacancy cluster but it is difficult to distinguish them with those of 500 °C, if we  
 283 consider the measurement discrepancy for such samples. Finally, and more remarkably, at the same

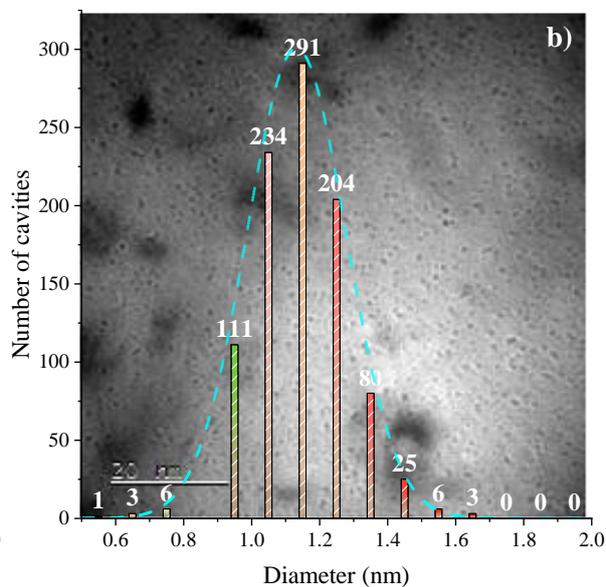
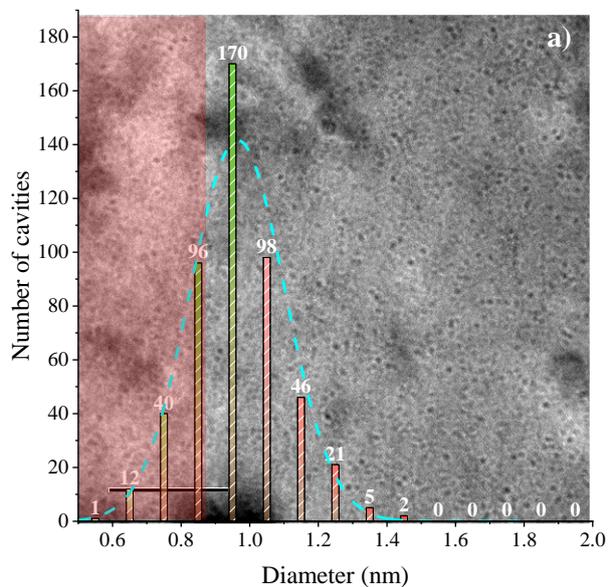
284 irradiation temperature, the  $SW$  points measured for the purest sample (6N-XHP) are the furthest  
285 away from the annihilation characteristics of the single vacancy, indicating that the fraction of  
286 positrons annihilated at vacancy clusters is greater in the 6N-XHP than in the 3N-HP sample. A straight  
287 line can be plotted to go through the fitted  $SW$  points in the samples irradiated at the same damage  
288 level (0.02 dpa) for 500 °C and 700 °C, which will be denoted  $D_3$ . When extending this line toward larger  
289  $S$  and lower  $W$  it can be observed that it joins the  $S_{V_N}$ ,  $W_{V_N}$  point corresponding to annihilation at the  
290 largest vacancy clusters detected in tungsten. When elongating  $D_3$  to the lower  $S$  and larger  $W$ , the line  
291 does not coincide with the lattice point but tends to two-thirds of the  $L_1$  straight line segment from the  
292 lattice point. As shown in Table 2, the estimated effective diffusion length  $L_{eff}^+$  of positrons in the  
293 damaged region is quite short (between 9 and 17 nm) for all irradiation conditions and tungsten  
294 purities. From equation 4, we can deduce a high trapping rate  $K$  of positrons of about  $1 \times 10^{12} \text{ s}^{-1}$  for  
295 the mean value of the estimated effective diffusion length  $L_{eff}^+$  of 13 nm. It follows that the fraction  
296 of positrons annihilated in the delocalized state, i.e. the perfect lattice, is negligible ( $< 1\%$ ). Moreover,  
297 the  $SW$  points of irradiated samples are located well below the annihilation characteristics of the  
298 largest vacancy clusters  $V_N$  containing 20 - 30 vacancies or with a diameter equal to or greater than 1  
299 nm. This indicates that positrons either detected mainly vacancy clusters with a diameter smaller than  
300 that of  $V_N$  –i.e. 1 nm- or that positrons are trapped and annihilate at different vacancy defects, i.e. the  
301 vacancy clusters  $V_N$  and a defect for which the annihilation characteristics  $SW$  are not yet known but  
302 which should be located on the  $D_3$  line. We will denote this defect  $D_x$  in the following discussion.  
303 Consequently, in the first case, the trapping rate is equal to  $K_{V_N}$  which means the trapping rate at  $V_N$   
304 vacancy clusters (which are smaller than  $V_N$  ones). In the second case,  $K$  is the sum of two trapping  
305 rates,  $K_{V_N}$ , for trapping at  $V_N$ , and  $K_{D_x}$  for trapping at  $D_x$ . We will discuss both cases in section 4.

### 306 **3.2 TEM results**

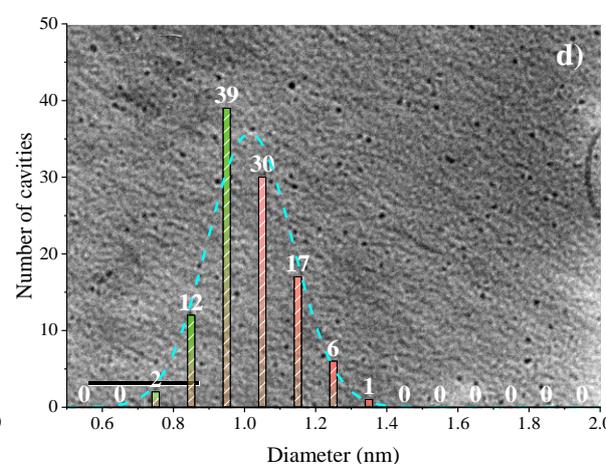
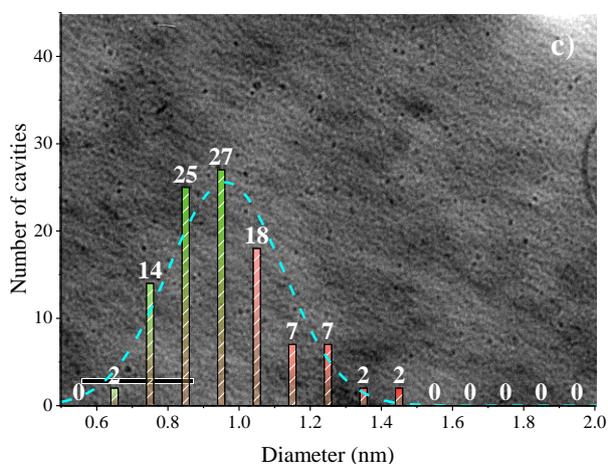
307 To characterize the larger vacancy-type defects, i.e. cavities, we directly performed observations using  
308 two different TEM microscopes with the same acceleration voltage and comparable magnification.  
309 Figure 4 shows the typical over-focused images (+300nm) of the 3N-HP and 6N-XHP tungsten samples

310 self-irradiated to 0.02 dpa at 500 °C and 700 °C. The identification and counting of the cavities were  
311 performed in only one over- and under-focused image pair for the samples irradiated at 500°C (Figure  
312 4 a-b). For the samples irradiated at 700 °C, the over- and under-focused images were recorded in  
313 several adjacent zones in the same grain, and the cavities were counted in 4 images (Figure 4 c-f) for  
314 3N-HP and 2 images (Figure 4 g-h) for 6N-XHP to ensure a reliable statistical analysis. For the 3N-HP  
315 sample irradiated at 500 °C, because of a low contrast quality, an area with a low distribution of cavities  
316 included in the 20 nm on the left side of figure 4a (red mask) was not taken into account and was  
317 removed from the probed volume. The size distribution of cavities, i.e. the number counted as a  
318 function of the diameter measured, was plotted and superimposed on the images in Figure 4. A total  
319 number of 491 and 479 cavities were counted for the 3N-HP sample irradiated at 500 °C and 700 °C  
320 respectively, and 1015 (500 °C) and 346 (700 °C) for the 6N-XHP one. Table 3 summarizes the mean  
321 diameters and the density of counted cavities in 3N-HP and 6N-XHP for both irradiation temperatures.  
322 The centroid of a Gaussian fitting was considered as the mean diameter of the cavities. The effective  
323 analyzed surface was multiplied by the corresponding thickness to assess the volumetric density of the  
324 cavities in the probed region. The corresponding errors on the diameter and density were estimated  
325 by using equations 1 and 2 in section 2.2.2. For irradiation at 500 °C, the cavity density was comparable  
326 for both purities at about  $1.6 \pm 0.5 \times 10^{24} \text{ m}^{-3}$ . It remained very close for both purities when the  
327 irradiation temperature increased to 700 °C, but decreased by approximately a factor of 2 ( $0.65 \pm 0.5$   
328  $\times 10^{24} \text{ m}^{-3}$ ) for the highest temperature. Regarding the diameter, whatever the irradiation temperature,  
329 the mean value of the 3N-HP sample (about 0.97 nm) was slightly lower than that of the 6N-XHP sample  
330 (1.13 - 1.22 nm for 500 °C and 700 °C, respectively). Furthermore, a large number of cavities with a  
331 diameter above 1 nm were counted in the 6N-XHP sample (82 % for 500 °C and 87 % for 700°C), in  
332 contrast to the 3N-HP samples (22 %, for 500 °C and 36 % for 700 °C). This indicates that larger cavities  
333 are observed in 6N-XHP samples for both irradiation temperatures (500 and 700 °C) as is clearly shown  
334 in Figure 5, where the total cavity size distributions are plotted for all the samples for the irradiations  
335 performed at 500°C (Figure 5a) and 700°C (Figure 5b). Besides, assuming that the cavities are spherical,

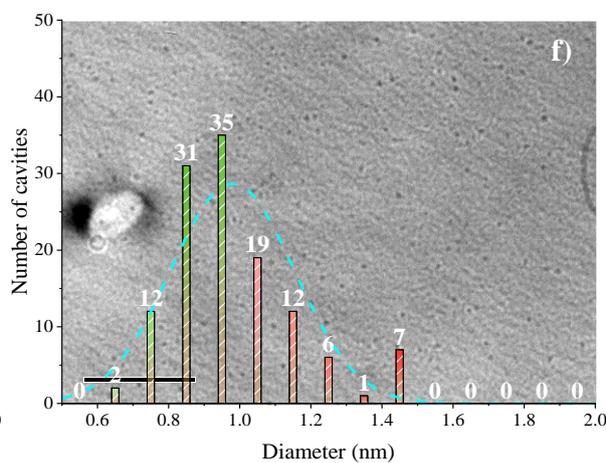
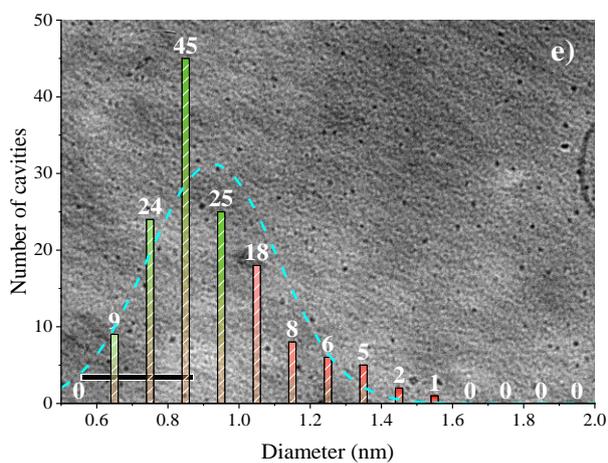
336 the local swelling due to cavities was estimated by dividing the total volume of the cavities counted by  
 337 the total analyzed volume. The local swelling due to cavities was estimated to be between  
 338 approximately 0.1 % in 6N\_XHP irradiated at 500 °C and 0.04 % for 3N-HP irradiated at 700 °C. For both  
 339 irradiation temperatures, larger local swelling was obtained in 6N-XHP samples than in 3N-HP ones.



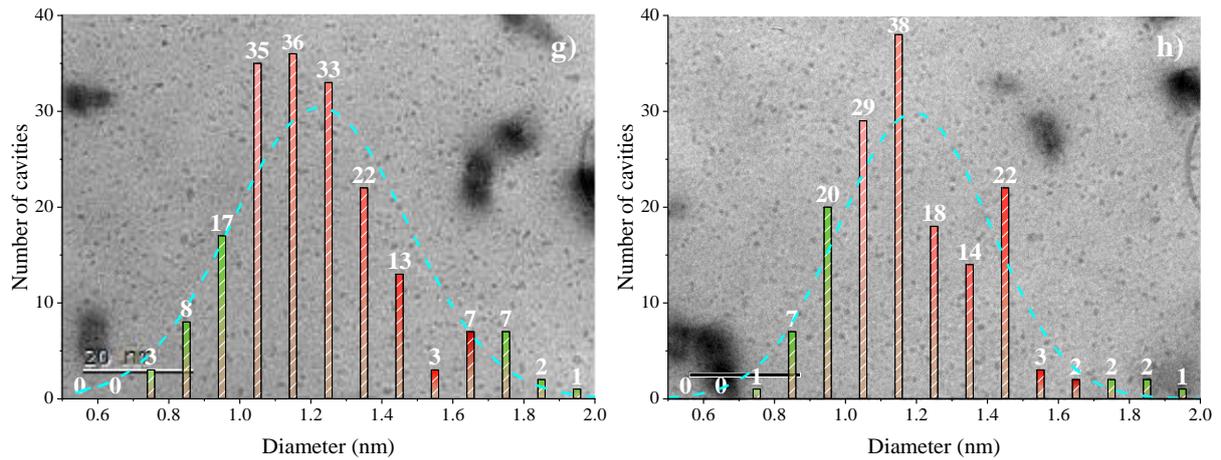
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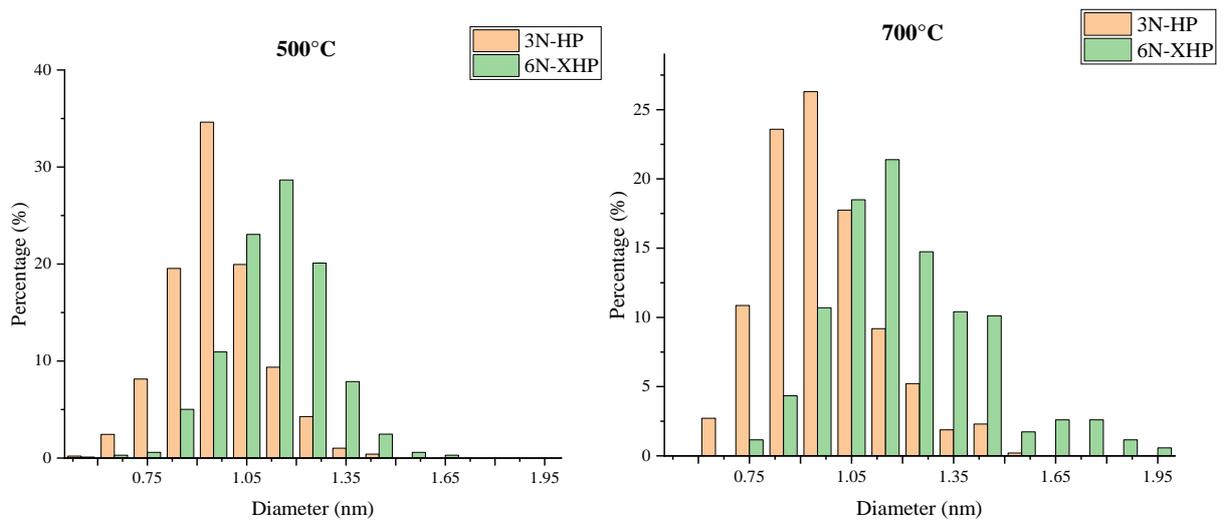
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343  
 344 *Figure 4: Over focused (+300 nm) images a) 3N-HP sample and b) 6N-XHP sample irradiated at 500 °C (0.02 dpa)*  
 345 *observed by a JEOL ARM200F cold field emission gun microscope and Over-focus (+300 nm) image c-f) 3N-HP*  
 346 *sample and g-h) 6N-XHP sample irradiated at 700 °C (0.02 dpa) observed by a Philips CM20 microscope. The size*  
 347 *distributions of cavities are superimposed on their respective images and were fitted by a Gaussian function*  
 348 *(cyan dashed line).*



349  
 350 *Figure 5: Histogram of the size of cavities in 3N-HP and 6N-XHP samples irradiated at 500 °C (left) and 700 °C (right) to 0.02*  
 351 *dpa*

Damage level (dpa)	0.02			
Observation conditions	JEOL ARM200, 200 kV, 500 kX,		Philips CM20, 200 kV, 500 kX	
Irradiation Temperature (°C)	500		700	
Purity	3N-HP	6N-XHP	3N-HP	6N-XHP
Thickness (nm)	55 ± 20 (EFTEM)	90 ± 30 (EFTEM)	35 ± 20 (evaluated)	60 ± 50 (evaluated)
Mean diameter(nm)	0.97 ± 0.19	1.13 ± 0.21	0.97 ± 0.25	1.22 ± 0.25
Density (10 <sup>24</sup> m <sup>-3</sup> )	1.73 ± 0.71	1.56 ± 0.52	0.70 ± 0.42	0.60 ± 0.53
Swelling %	0.09 ± 0.02	0.12 ± 0.04	0.04 ± 0.02	0.08 ± 0.05

352 *Table 3: The mean diameters of cavities observed by TEM and their density in irradiated 3N-HP and 6N-XHP*

353 *samples and the measured or evaluated thickness*

#### 354 **4. Discussion**

355 PAS exhibits the formation of vacancy-type defects in self-irradiated tungsten at a low damage dose of  
356 0.01 to 0.02 dpa. The nature of these defects changes with the irradiation temperature and whereas  
357 mainly single vacancies are detected for irradiation at RT, a large fraction of positron annihilates as  
358 trapped at vacancy clusters when irradiation is performed at 500 and 700°C. TEM observations  
359 confirmed the presence of cavities for these irradiation conditions. The formation of the vacancy  
360 clusters or cavities is probably the result of the migration of single vacancies of tungsten and their  
361 agglomeration which becomes possible at such high temperatures considering the migration energy  
362 of the single vacancy ( $E_m(V)=1.66\text{eV}$  [31]). This agglomeration has been already observed after the  
363 annealing of irradiated tungsten with 800 keV <sup>3</sup>He at RT when the annealing temperature exceeds  
364 350 °C [38,51]. As explained in section 3.1, the *SW* values obtained in samples irradiated at 500 and  
365 700 °C could correspond to either 100 % of annihilation in vacancy clusters with a diameter below 1  
366 nm, or to a competition of annihilation in at least two types of vacancy defects, i.e. the vacancy clusters  
367  $V_N$  and a defect  $D_x$  for which the annihilation characteristics are not yet known and which should be  
368 located on the  $D_3$  line. TEM detects vacancy clusters or cavities with a mean diameter of about 1 nm,  
369 which eliminates the first hypothesis. It can be concluded that the positrons are sensitive to a defect  
370  $D_x$  that cannot be detected in TEM. It follows that the differences between the PAS results obtained in  
371 3N-HP and 6N-XHP samples can be explained by a lower fraction of annihilation in the vacancy clusters  
372  $V_N$  in 3N-HP than in 6N-XHP, in other words, a higher fraction of annihilation in  $D_x$  is revealed in 3N-HP

373 samples. The nature of these defects is discussed in the following. First, since the two techniques show  
374 that the agglomeration of small vacancies was impeded in 3N-HP samples compared to 6N-XHP ones,  
375 it is reasonable to pay attention to the LEs in the samples, such as H, C, N and O considering their  
376 properties in tungsten and their strong interactions with vacancy-type defects (see Table 1). As shown  
377 in Table 4, since the 6N-XHP was analyzed by LA-ICP-MS, the quantity of the LEs could not be detected.  
378 Regarding the 3N-HP sample, an obvious and large quantity of LEs was recorded, suggesting a higher  
379 concentration of LEs that ranges between 130 to 910 at. ppm, within in particular 460 at. ppm of  
380 carbon in 3N-HP samples. These LEs have low migration energy in tungsten, which indicates their high  
381 mobility under the irradiation conditions performed in this study. Furthermore, they can be linked  
382 firmly with a single vacancy leading to the formation of V-LE complexes owing to their high binding  
383 energy. Thus, such V-LE complexes could be formed in tungsten when the irradiation temperature is  
384 high enough to allow the migration of either LEs or of the single vacancies, which is the case for both  
385 from 500°C. In these complexes, the most favorable occupation site for C, N, and O atoms is in the  
386 vicinity of a single vacancy, at a distance of about 1.3 Å from the vacancy's center close to an octahedral  
387 site [25,26,29]. Their theoretical dissociation energies are given in Table 4, i.e. the sum of the migration  
388 of the most mobile species of the complexes and the binding energies. A high value was calculated for  
389 carbon (3.39 eV), nitrogen (3.21 eV), and oxygen (3.22 eV), but it was only 1.4 eV for hydrogen.  
390 Consequently, for the cases of C, O, and N, the complexes should be stable even though the irradiation  
391 is performed at 500 °C and 700 °C, whereas the V-H complexes should be dissociated at high  
392 temperatures. However, such complexes cannot be detected by TEM because of their size. Positrons,  
393 however, should be sensitive to these complexes because the LE atoms are not trapped in the center  
394 of the vacancy and leave some space with a lower electron density than in the lattice of the W. The  
395 annihilation characteristics  $S_{Dx}$  and  $W_{Dx}$  of these complexes should be different from those of single  
396 vacancies and manifested by a lower  $S$  and higher  $W$  due to the electronic density which is higher in  
397 the complex than in an empty single vacancy. Therefore, the  $S_{Dx}$ ,  $W_{Dx}$  point should be on the lower part  
398 of the  $D_3$  line.

$X$	at. ppm		$E_m^X$ (eV)	$E_b^{V-X_1}$ (eV)	$E_{diss}^{V-X_1}$ (eV)
	3N-HP	6N-XHP			
H	910	Ud	0.21 (TIS-TIS) [27]	1.24 [28]	1.45
C	460	Ud	1.46 (TIS-OIS) [23]	1.93 [23]	3.39
N	130	Ud	0.73 (TIS-OIS) [29]	2.48 [24]	3.21
O	345	Ud	0.17 (TIS-TIS) [25]	3.05 [25]	3.22

399 *Table 4: Elementary composition in the 3N-HP and 6N-XHP sample from the supplier (Ud: undetectable), and*  
400 *the most favorable calculated value of migration energy  $E_m^{X_1}$  of element X and its binding energy  $E_b^{V-X_1}$  with a*  
401 *tungsten single vacancy. The most favorable inter-site migration (TIS: tetrahedral interstitial site, OIS:*  
402 *octahedral interstitial site). The dissociation energy of the V- $X_1$  complex is  $E_{diss}^{V-X_1} = E_m^i + E_b^{V-X_1}$  where i is the*  
403 *most mobile species between V and X.*

404 The formation of these V-LE complexes could be more efficient in the less pure material (3N-HP) than  
405 in the purer one (6N-XHP). These complexes could impede the migration of some single vacancies that  
406 can migrate and join the vacancy clusters, contributing to their growth in the less pure tungsten (3N-  
407 HP), as it has been shown in carbon-doped Fe for the V-C complex [24]. In addition, Asoka-Kumar et al.  
408 [52] and Rementeria et al. [53] showed two examples of the effect of the C trapping at vacancies on  
409 the electron momentum distribution probed by positrons in Fe based alloys, in fatigued type 304  
410 stainless steel and in bainite phase of Fe-0.66C-1.45Si-1.35Mn-1.02Cr-0.10Ni-0.24Mo alloy  
411 respectively. The carbon effect was evident at around  $10 \times 10^{-3} m_0C$ , which is included in the W region  
412 of our SPB-DB measurement.

413 The nature of the complexes cannot be determined from the data presented in this study. It could be  
414 V- $C_n$ , V- $N_n$ , V- $O_n$ , or V-C-H as predicted by simulation, although the number of LE atoms in the  
415 complexes cannot be specified. Nevertheless, the number of bound LEs n should be low enough to  
416 make positron trapping at V-LE complexes still possible. If we consider the density of vacancy clusters  
417 or cavities  $V_N$  observed in TEM of about  $(1.6 \pm 0.5) \times 10^{24} m^{-3}$  and the trapping coefficient of the positron  
418 at  $V_N$  of about  $1.6 \times 10^{-13} m^3 \cdot s^{-1}$  as given in reference [46], then the trapping rate at  $V_N$  can be estimated  
419 to be about  $3 \times 10^{11} s^{-1}$ . From the total trapping rate estimated from the positron effective diffusion  
420 length, the trapping rate at defects  $D_x$  is  $5 \times 10^{11} s^{-1}$ . Considering that the trapping coefficient at defects

421  $D_x$  is close to that of single vacancies, i.e.  $\mu_V = 6 \pm 3 \times 10^{-15} \text{ m}^{-3} \cdot \text{s}^{-1}$  [46], the concentration of  $D_x$  could be  
422 about  $7 \times 10^{25} \text{ m}^{-3}$  (i.e. about 1200 at. ppm). These values are of the same order of magnitude as the  
423 total C, N, and O concentrations in 3N-HP samples (935 at. ppm).

## 424 **5. Summary**

425 In this work, we performed PAS and TEM to characterize the vacancy-type defects induced by self-  
426 irradiation in tungsten as a function of its purity and the irradiation temperature. The two techniques  
427 consistently indicate a clear effect of the purity on the vacancy-type defect behaviors as a function of  
428 irradiation temperature. At RT, PAS characterization revealed an equivalent homogenous distribution  
429 of small vacancy clusters in the samples of two different purities. However, an obvious purity effect  
430 was observed at 500 °C and 700 °C with the damage level (0.02 dpa). TEM characterization showed  
431 larger cavities in the higher purity samples than in the lower purity ones, with a drastically increasing  
432 number of cavities with diameters above 1 nm. The PAS results revealed at least two different positron  
433 traps: (1) large vacancy clusters  $V_N$  and (2)  $D_x$  vacancy defects. A greater fraction of annihilation at  
434 defects  $D_x$  was observed in lower purity samples. These consistent results can be compared to the  
435 properties of the LEs (carbon, oxygen, nitrogen) in tungsten and in particular to their high propensity  
436 to be bound to a single vacancy. This could suggest that the formation of V-LE complexes could impede  
437 the clustering of vacancies in lower purity material. Further annealing experiments and qualitative  
438 measurements such as positron lifetime spectroscopy (PALS), atom probe tomography (APT), or SIMS  
439 will be performed to identify in greater detail the nature of the complexes.

## 440 **Credit authorship contribution statement**

441 **Zhiwei Hu**: Sample preparation, SPB-DB experiment, PAS and TEM data processing and analysis,  
442 Writing – original draft & editing. **Pierre Desgardin**: Supervision, SPB-DB equipment **Cécile Genevois**:  
443 Supervision, TEM experiments **Jérôme Joseph**: Sample preparation and equipment support **Brigitte**  
444 **Décamps & Robin Schäublin**: TEM analysis methodology and in situ irradiations **Marie-France Barthe**:  
445 Conceptualization, contribution to the in situ irradiations, supervision, review & editing.

## 446 **Declaration of Competing Interest**

447 The authors declare that they have no known competing financial interests or personal relationships  
448 that could have appeared to influence the work reported in this paper.

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