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Development of Positron Annihilation Spectroscopy for Characterizing Neutron Irradiated Tungsten

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Development of positron annihilation spectroscopy for characterizing neutron irradiated tungsten

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Abstract

Tungsten samples (6 mm diameter, 0.2 mm thick) were irradiated to 0.025 and 0.3 dpa with neutrons in the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory as part of the US/Japan TITAN collaboration. Samples were then exposed to deuterium plasma in the Tritium Plasma Experiment (TPE) at 100, 200 and 500ºC to a total fluence of 1 x 10^{26} m^{-2}. Nuclear reaction analysis (NRA) and Doppler broadening positron annihilation spectroscopy (DB-PAS) were performed at various stages to characterize radiation damage and retention. We present first results of neutron irradiated tungsten characterized by DB-PAS in order to study defect concentration. Two positron sources, ^{22}Na and ^{68}Ge, probe ~58 μm and through the entire 200 μm thick samples, respectively. DB-PAS results reveal clear differences between the various irradiated samples. These results, and a correlation between DB-PAS and NRA data are presented.

Keywords: Neutron, Defects, Tungsten, Doppler broadening positron annihilation spectroscopy, Plasma-facing components
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1. Introduction

Plasma-facing materials (PFM) in next step fusion devices will be exposed to high ion and neutron fluxes resulting in material damage. For example, ITER expects to reach a lifetime neutron fluence on the order of 3 x 10^{24} m^{-2} with tungsten damage approaching 0.6-0.7 dpa [1]. Hydrogen isotopes are retained at material defects (e.g., vacancies, vacancy clusters, grain boundaries), and as opposed to ion-induced defects, which reside within the first few microns, neutrons produce damage throughout the depth of the material. Accurately estimating retention of tritium in neutron irradiated tungsten is a key issue for both fuel control and fusion safety.

Positron annihilation spectroscopy (PAS) is used to investigate defects within materials. Various PAS techniques exist [2] and the most prominent include lifetime spectroscopy, angular correlation PAS, and Doppler broadening (DB) PAS [3]. Of these, DB-PAS is the most straightforward since it can be performed using a single high purity Ge (HPGe) detector without the need of high speed coincidence electronics [4]. PAS has become widely used in materials engineering, yet relatively few PAS studies have been conducted on tungsten plasma-facing components (PFC). To the authors' knowledge, we present the first known results using DB-PAS to study neutron irradiated tungsten exposed to hydrogen isotope plasmas.

PAS is an attractive diagnostic for fusion materials for several reasons. 1) PAS is capable of detecting defects over a very wide range of sizes in bulk materials, from monovacancies to large clusters, 2) Depth resolution of 10-100's μm can be obtained using multiple positron sources, 3) Hydrogen decorated voids can be distinguished from empty voids, and 4) In-situ analysis can be performed to dynamically interrogate samples.

We present initial results using DB-PAS, and show how these data relate to deuterium concentration as measured by nuclear reaction analysis (NRA). This paper is organized as follows. First the experimental setup of samples and analysis techniques are presented. Section three shows and discusses the DB-PAS results from various damaged tungsten samples. These DB-PAS results are then compared to NRA data for the same samples to obtain a preliminary relationship between *S*-parameter and deuterium concentration in neutron irradiated tungsten.

2. Experimental details

2.1. Sample preparation

Under the 2007-2012 US/Japan Tritium, Irradiation and Thermofluids for America and Nippon (TITAN) collaborative agreement, tungsten samples were cut from a 99.99 at. % purity (A.L.M.T. Corp) 6 mm rod into 0.2 mm thick disks. Samples were mechanically polished and annealed to 900ºC for 30 min. Samples were then shipped to Oak Ridge National Laboratory to be irradiated in the High Flux Isotope Reactor (HFIR). Neutron thermal and fast fluxes were 2.5 x 10^{19} n/m^2s and 8.9 x 10^{18} n/m^2s, respectively [5]. In order to reach 0.025 dpa, samples were irradiated for 33.8 hr, and 0.3 dpa required 391 hr. Under the 2013-2018 US/Japan collaboration, PHENIX, a thermal neutron shielding (e.g., europium oxide) will be used to selectively irradiate W samples in HFIR

with fast neutrons to better replicate fusion neutron damage (see Ref. [6] for a comparison of damage production with thermal, fast, and fusion neutrons). Temperature during neutron irradiation was maintained at reactor coolant temperature (50-70ºC). Subsequent analyses (see next section) commenced after sample radioactivity and dose rate cooled to a manageable level.

Deuterium was implanted in several samples at the Idaho National Laboratory (INL) in the Tritium Plasma Experiment (TPE), which is among the few facilities capable of performing tritium seeded plasma experiments on neutron activated PFC materials [7]. Sample temperature was maintained at 100, 200, and 500ºC during implantation with a low energy (100 eV) deuterium flux of 5×10^{21} $m^{-2}s^{-1}$. To ensure deuterium saturation of the near surface neutron induced defects, multiple irradiations were performed at fluence increments of 5×10^{25} m^{-2}, with various analyses performed intermittently.

A total of nine samples were used throughout the present work. Due to the difficulty of obtaining neutron irradiated tungsten samples, and to maximize the comparison presented here, our analysis includes samples from previous experimental campaigns. Specifically, the 0.025 dpa samples underwent thermal desorption [5,8] prior to DB-PAS scans, whereas the 0.3 dpa samples had DB-PAS performed prior to thermal desorption (discussed further in context of ***Figure 2***-3).

2.2. Analysis techniques

2.2.1. Doppler-broadening positron annihilation spectroscopy theory and setup.

Positrons introduced into a material thermalize within about 10 psec through a series of interactions with localized electric fields in the material [9]. The positively charged positron is repelled by the ionic cores of atoms, scattering until the positron eventually annihilates with an electron. If along its 10-1000 μm trajectory (passing some ~10^6 lattice sites) the positron randomly migrates into a void, the positive ionic cores of the void surface repel the positron, thus "trapping" it in the void [2]. The lifetime of trapped positrons is a few 100 psec longer than other positrons, making this technique very sensitive to voids of any size, including monovacancies.

The annihilation of a positron with an electron produces two 511 keV photons. For momentum to be conserved, the annihilation photons experience a Doppler shift corresponding to the electron binding energy [9]. Core electrons are bound more tightly than valence electrons and cause a larger shift than positron annihilation with valence electrons. Since positrons trapped in defects are more likely to annihilate with valence electrons than core electrons, DB-PAS spectra of samples with more defects produce a sharper 511 keV central peak [10], and samples with fewer defects have a broader 511 keV peak. Doppler broadening is lessened for samples with more trapping sites [11].

Our DB-PAS software controls the HPGe detector and is set to collect a spectrum until a nominal 10^6 annihilation events are collected within the region of interest (ROI). The ROI is centered at 511 keV and spans 20 keV. The *S* (sharpness) parameter is calculated from this event spectrum as the ratio of the counts from the center channels (510.1 keV to 511.9 keV) divided by total number of counts in the ROI. Samples with more defects have a larger *S*-parameter value. The *S*-parameter uncertainty is governed by the standard deviation of repeated measurements [12], and is found to be ±0.0007.

A ^{60}Co source is mounted to the HPGe detector to provide a constant reference (1332 keV line) signal to correct for electronic drift. The resolution for the detector is 1.8 keV full width half max (FWHM) for ^{60}Co (1332 keV). The sample and positron source are positioned 6.2 cm away from the detector, and the detector deadtime is ~30-40%. The *S*-parameters measured in this work are sensitive to the spatial configuration of sample, source, and detector.

Positron sources used in the present experiments included ^{22}Na (2.6 year half-life, 0.545 MeV maximum energy, 0.26 MeV mean energy) and ^{68}Ge (275 day half-life, 1.88 MeV maximum energy, 0.41 MeV mean energy). Unmoderated radioactive positron sources have a continuous energy spectrum. Consequently, the mean energy of this energy spectrum is often used to calculate the penetration depth in samples. We have chosen the method by Mourino et al. to calculate positron penetration depth [13], which takes into account material density, atomic number, and the positron mean energy [14].

Eight PAS spectra were collected for each sample using ^{22}Na and ^{68}Ge on the front and back faces, each scan repeated twice for improved statistics. ***Figure 1*** shows the calculated implantation profile for our 200 μm thick tungsten samples using the formula from Mourino, et al. [14]. At a depth of 58.7 μm, 95% of ^{22}Na positrons annihilate in our tungsten samples, and less than 0.004% of positrons survive at a depth of 200 μm. Accordingly, ^{22}Na PAS scans of the sample's back face do not contribute to spectra collected from the front face, and vice versa. For ^{68}Ge, 82% of positrons have annihilated at a depth of 200 μm, therefore defects throughout the entire sample contribute to the spectrum and one would expect front and back face spectra to be similar.

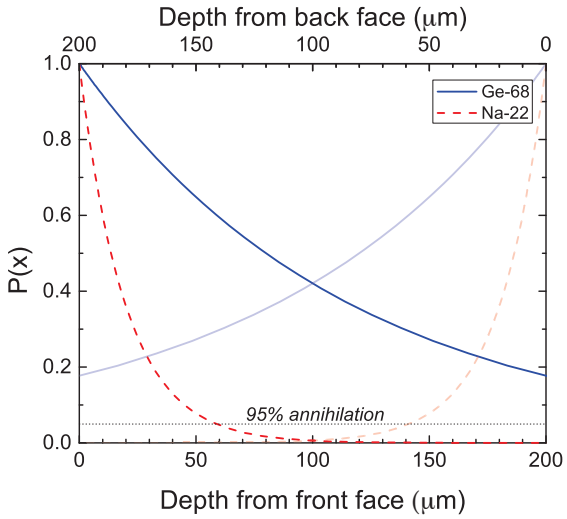

Figure 1. Calculated implantation profile of ^{22}Na and ^{68}Ge positrons in tungsten.

2.2.2. Nuclear reaction analysis

Deuterium concentration in tungsten (atomic fraction, D/W), as a function of depth, was obtained for this study by NRA conducted at the Ion Beam Laboratory at the University of Wisconsin-Madison. A 3.5 MeV ^{3}He beam is used to produce D-^{3}He fusion according to the D(^{3}He, p)^{4}He nuclear reaction, in which protons are detected to

determine the deuterium concentration in the sample. The SIMNRA software is used to interpret the results. A virgin tungsten sample (i.e., no neutron irradiation and no ion implantation) is scanned multiple times with NRA to set a baseline for calibrating the SIMNRA software. In order to more meaningfully compare NRA results to DB-PAS data, we assume that defects are saturated with deuterium and a deuterium concentration is proportional to defect concentration.

3. Results and discussion

3.1. DB-PAS results

The *S*-parameter from various samples analyzed using ^{68}Ge and ^{22}Na on the front and back faces is shown in ***Figure 2***. The *S*-parameter is plotted with respect to the displacement damage (displacements per atom – dpa) from HFIR neutron irradiation, and the symbol shape indicates the temperature at which the sample was exposed to TPE deuterium plasma irradiation. The same nine tungsten samples are represented in each pane. Of the nine samples, two have no neutron damage, four samples have 0.025 dpa, and three samples have 0.3 dpa (refer to x-axis). PAS was performed after the samples had undergone a repeated sequence of TPE plasma exposure and NRA.

As calculated in ***Figure 1***, ~18% of ^{68}Ge positrons penetrate the full 200 μm depth of the tungsten sample, and consequently positrons from the front side and the back side probe the same bulk region. One would anticipate the *S*-parameters from the front and back faces of the sample to be similar. Indeed, ***Figure 2*** (a) and (b) show very similar *S*-parameters for the front and back face of each sample, where the front faces have slightly larger *S*-parameters. This is because, even though a portion of ^{68}Ge positrons penetrate through the thickness of the samples, more positrons annihilate near the entering face, and the front face was exposed to TPE plasmas. In panes (a) and (b), the *S*-parameters (and consequently defect concentration) increase as dpa and TPE irradiation temperature increase.

Using ^{22}Na, the *S*-parameters from the front and back faces are expected to be different since deuterium was implanted in the front face via TPE plasma. Interestingly, the *S*-parameter for 0.3 dpa samples in ***Figure 2*** (c) and (d) is less on the front plasma-exposed face than the back face, when it was expected that plasma exposure would induce further damage (larger *S*-parameter) on the front face. This is explainable since the 0.3 dpa samples did not undergo thermal desorption and the defects are assumed to be saturated with deuterium [5,15]. The neutron-induced voids on the front face have a higher electron density than the empty voids on the back face, and consequently a lower *S*-parameter. ‘t Hoen et al. report little difference in the *S*-parameter between two self-damaged W samples where one sample was also exposed to deuterium plasma, however the D-implanted sample consistently has a lower *S*-parameter until high desorption temperatures are reached (see Fig. 6 in [16]). Furthermore, Nambissan and Subrahmanyam observed similar behavior in alpha irradiated tungsten; that is, the *S*-parameter was lower while voids were impregnated with impurities (i.e., helium), and the *S*-parameter increased during desorption before defects annealed [17,18]. Elemental discrimination of empty voids and impurity decorated voids is possible through coincident DB-PAS [9] and will be examined in future work.

Another interesting observation in ***Figure 2*** is that the defect concentration increases as the dpa increases for each isochronal set of samples. The measured *S*-parameters for samples with no exposure to TPE plasma (black squares) do not increase appreciably from 0.025 to 0.3 dpa with ^{22}Na positions (c-d), but do with ^{68}Ge positrons (a-b). This indicates that within the first ~58 μm (the probing depth of ^{22}Na positrons) the defect concentration doesn't change much between 0.025 and 0.3 dpa; however, at a depth of 50-150 μm, the defect concentration is larger for 0.3 dpa samples than 0.025 dpa samples. The positron phenomena that could be playing a role in this, such as surface effects [19], chemical and elemental influence on Doppler broadening [9], and impurity decoration of voids [20,21], need additional investigation.

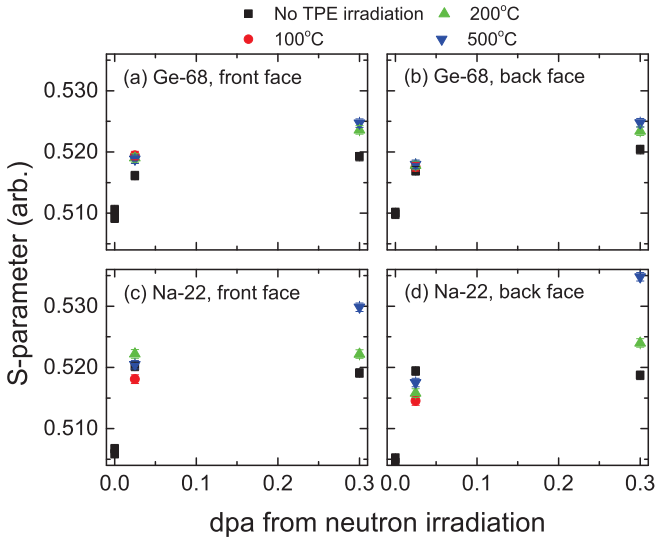

Figure 2. S-parameters collected from 9 different samples. The S-parameters from (a) the front face, and (b) the back face of the tungsten samples are nearly identical when probed with ^{68}Ge positron source. However, when using ^{22}Na positrons, which have a much shallower penetration depth, the front plasma-exposed face (c) surprisingly shows 0.3 dpa samples have a lower S-parameter than corresponding measurements from the back face (d).

3.2. Correlation between *S*-parameter and NRA measurements

As state previously, in order to more meaningfully compare NRA results to DB-PAS data, we assume that defects are saturated with deuterium and the deuterium concentration is proportional to defect concentration. In the case of tungsten this may not be an inaccurate assumption. As discussed in Wampler and Doerner [22], at low temperatures, implanted deuterium atoms in tungsten will nearly saturate existing defect sites prior to diffusing deeper into the material. This is due to the high energy well associated with tungsten defect sites. For this work, NRA data [5] were collected from five of the nine samples shown in ***Figure 2***. The *S*-parameters of these samples are plotted in ***Figure 3*** with respect to the averaged NRA deuterium concentrations from 0-5 μm. The *S*-parameters were collected from the front face of the sample using ^{22}Na since this is the region closest to that probed by NRA. The virgin sample (W311) was prepared

as described in Section 2.1 and had no further modification or analysis prior to DB-PAS. For the purpose of including the virgin tungsten sample scanned in this study, we used the intrinsic trap concentration of 15 atomic parts per million (appm) reported in ref. [22] as a pseudo deuterium concentration. Figure 3 contains this comparison.

As can be seen, sample Y112 deviates significantly from the trend suggested by the other samples. At higher implantation temperatures (e.g., 500 ºC), defects are likely not saturated, and work by Shimada et al. suggests they are ~30-40% saturated [5]. The high *S*-parameter for Y112 indicates that it has a significant concentration of defects, and its low deuterium concentration suggests that the voids in this sample are << 30% saturated.

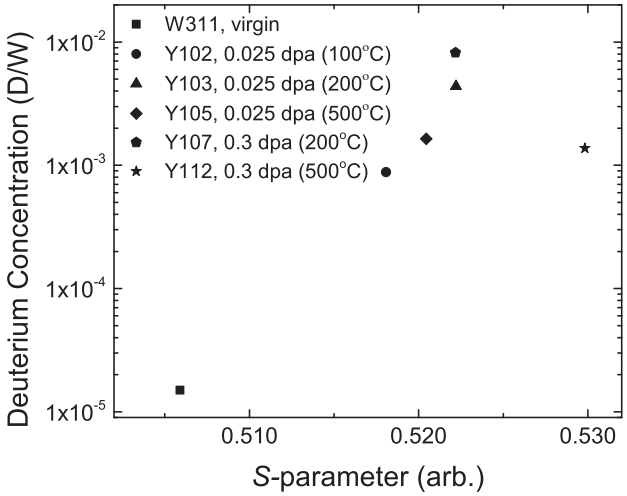

Figure 3. Deuterium concentration (D/W) plotted with respect to S-parameter. The intrinsic trap concentration given in [22] is used for virgin sample W311. We postulate that trap sites in sample Y112 are << 30% saturated.

4. Conclusions

Doppler broadening positron annihilation spectroscopy (DB-PAS) has been used to investigate defects and deuterium retention in neutron irradiated tungsten. Following neutron irradiation, deuterium was implanted in samples at 100, 200, and 500ºC in the tritium plasma experiment (TPE), and subsequently analyzed using NRA and DB-PAS. Positrons from a ^{68}Ge source probe the entire 200 μm thickness of our samples and qualitatively reveal increasingly numerous defects as dpa and TPE irradiation temperature increase. Positrons from a ^{22}Na source penetrate ~58 μm into the samples and show striking differences between the plasma-exposed front- and back-faces. The *S*-parameter was plotted with respect to NRA measured deuterium concentrations, providing a preliminary relationship between the two measurements. Neutron damage occurs throughout the bulk material of PFCs, and DB-PAS appears to be ideal for measuring bulk defects and hydrogen isotope retention. This is especially important for addressing tritium permeation in neutron irradiated tungsten.

Future work will examine the effect of partial trap saturation through thermal desorption experiments. We also plan to measure defect concentration with a technique

more commensurate with the probing depth of DB-PAS to be used in developing a calibration for the *S*-parameter.

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