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Hydrogen Interaction with Vacancies in Electron Irradiated Niobium

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Defect studies of Nb irradiated with 10 MeV electrons were performed in the present work by means of positron annihilation spectroscopy. The lattice defects were characterized by positron lifetime spectroscopy. Moreover, defect depth profiles were studied by slow positron implantation spectroscopy. The experimental investigations were accompanied by first principles theoretical calculations of positron parameters. It was found that irradiation-induced vacancies in Nb specimens are surrounded by H, which causes a shortening of the lifetime of trapped positrons. The influence of a Pd and Cr over-layer on the H concentration in the Nb specimens was examined.

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1. Introduction

Nb is an important material for high temperature technology, and for advanced fission and fusion reactors. The information about irradiation-induced defects in Nb is highly important for these applications. Nb is known to uptake easily H [1], which is very mobile already at room temperature [2], and may interact with irradiation-induced defects. The knowledge about H interaction with defects in metals is still limited despite an increasing effort given to such investigations especially on the atomic scale; see the recent review [3].

Positron annihilation spectroscopy (PAS) is a well established non-destructive method with very high sensitivity to vacancies and other open-volume

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defects [4] and proved itself to be a very powerful tool for investigations of H interaction with defects. Recently, it has been discovered by PAS that vacancies surrounded by H are introduced into Nb by electrochemical H loading [5].

Hautojärvi et al. [6, 7] employed PAS for investigations of defect recovery in Nb irradiated by 3 MeV electrons at liquid nitrogen temperature. The authors found that Nb specimens handled in a protective He atmosphere in order to prevent them from H contamination exhibited positron lifetime (LT) of irradiation-induced defects of (210±2) ps, while the same sample kept in air exhibited a shorter lifetime of (170±2) ps only. These experimental findings have been attributed to H trapped at irradiation-induced vacancies in the Nb sample kept in air. In the present work we continued with the investigations of H interaction with defects in electron irradiated Nb, started in Refs. [6, 7], and extended them in several aspects: (i) a high resolution LT spectrometer with timing resolution more than two times better than that in Refs. [6, 7] was employed. It enables to distinguish close spaced components corresponding to vacancies surrounded by various numbers of H atoms; (ii) defect depth profiles were studied by slow positron implantation spectroscopy (SPIS); and (iii) an enhancement of H uptake due to a thin Pd and Cr over-layer was examined. Positron characteristics obtained experimentally were compared with first principles theoretical modeling.

2. Experimental

Bulk Nb (99.9%) specimens were firstly annealed at 1000°C for 1 h in vacuum (10^{-3} mbar) to remove virtually all defects. The specimens were subsequently irradiated with 10 MeV electrons up to a fluence of 2×10^{21} m^{-2} ($T_{\rm irr} \leq 100$°C). The surface of the specimens was covered with a 30 nm thick Pd over-layer deposited by cold cathode beam sputtering in an UHV chamber (10^{-10} mbar). These specimens with a Pd cap sputtered *prior* to electron irradiation were compared with those having a Pd cap deposited *after* irradiation. Another set of specimens was covered with a 30 nm Cr over-layer instead of the Pd cap.

A ^{22}Na$_2$CO$_3$ positron source (≈ 1.5 MBq) deposited on a 2 μm thick mylar foil was used in LT measurements. This source was always forming a sandwich with two identically treated Nb specimens. The source contribution in LT spectra consisted of two weak components with lifetimes ≈ 368 ps and ≈ 1.5 ns, and corresponding intensities of $\approx 8\%$ and $\approx 1\%$. LT spectroscopy was performed using a fast-fast spectrometer [8] with a timing resolution of 160 ps (FWHM ^{22}Na). At least 10^7 positron annihilation events were accumulated at each LT spectrum which was subsequently decomposed using a maximum likelihood procedure [9]. SPIS studies were performed at the magnetically guided positron beam “SPONSOR” [10] with positron energy E adjustable from 0.03 to 36 keV. Doppler broadening of the annihilation line was measured by a HPGe detector with an energy resolution of 1.09 keV at 511 keV and evaluated using the S and W line shape parameters. The $S(E)$ dependences were fitted by the VEPFIT software package [11]. It has to be noted that all the S and W parameters shown in this paper were normalized to the bulk values S_0, W_0 measured on the annealed Nb specimen.

Theoretical calculations of positron parameters were performed on 256 Nb atom supercells using the atom superposition method (ATSUP) [12] with the enhancement factor parameterized by Boroński and Nieminen [13]. The lowest energy sites of H atoms in a Nb crystal containing a vacancy were determined by the effective medium theory (EMT) [14] and are described in detail in Ref. [5].

3. Results and discussion

3.1. Initial non-irradiated specimens

LT results are summarized in Table. The annealed Nb specimen exhibits a single-component spectrum with a lifetime $\tau_{\mathrm{B}} = 128$ ps, which agrees with the calculated bulk Nb lifetime of 126 ps. Thus, the annealed specimen can be considered as a "defect-free" material. No new defects detectable by LT spectroscopy were created by sputtering of Pd (or Cr) cap, see Table. The $S(E)$ curve measured on the annealed specimen is plotted in Fig. 1. The positron diffusion length $L_{+,\mathrm{B}} = (319 \pm 8)$ nm was obtained from fitting by VEPFIT.

TABLE

Summary of PAS results: lifetimes τ_i and relative intensities I_i resolved in positron lifetime spectra, the χ^2 (per degree of freedom) value for the fit, positron diffusion length L_+, the net concentration of the irradiation-induced defects c_{D} obtained from fitting of the $S(E)$ curves by VEPFIT in combination with Eq. (3), the concentrations of v–H and v–2H complexes, $c_{\mathrm{v-H}}$, $c_{\mathrm{v-2H}}$, calculated from the three-component decomposition of LT spectra using Eqs. (1), (2), and the hydrogen concentration c_{H} calculated from Eq. (4).

Nb specimen	Non-irradiated			Irradiated			
	well annealed	covered with Pd	covered with Cr	*bare*	Pd cap *after* irradiation	*with* Pd cap	*with* Cr cap
τ_1 [ps]	128.3(4)	128.0(5)	127.6(6)	43(8)	44(9)	52(7)	48(5)
I_1 [%]	100	100	100	14(2)	14(2)	17(1)	15(2)
τ_2 [ps]	–	–	–	182 FIX	182 FIX	182 FIX	182 FIX
I_2 [%]	–	–	–	61(2)	57(2)	71(2)	74(1)
τ_3 [ps]	–	–	–	204 FIX	204 FIX	204 FIX	204 FIX
I_3 [%]	–	–	–	25(3)	29(4)	12(3)	11(9)
χ^2	1.05	1.04	1.06	1.08	1.05	1.07	1.06
L_+ [nm]	319(8)	300(10)	300(10)	178(6)	175(7)	190(10)	200(10)
c_{D} [10^{-5} at.$^{-1}$]	–	–	–	17(4)	19(4)	14(6)	12(4)
$c_{\mathrm{v-H}}$ [10^{-5} at.$^{-1}$]	–	–	-	4.7(6)	5.3(9)	1.8(5)	1.8(5)
$c_{\mathrm{v-2H}}$ [10^{-5} at.$^{-1}$]	–	–	–	11.0(7)	10.0(7)	10(1)	12(1)
c_{H} [10^{-5} at.$^{-1}$]	–	–	–	26.7(9)	25(1)	22(1)	26(1)

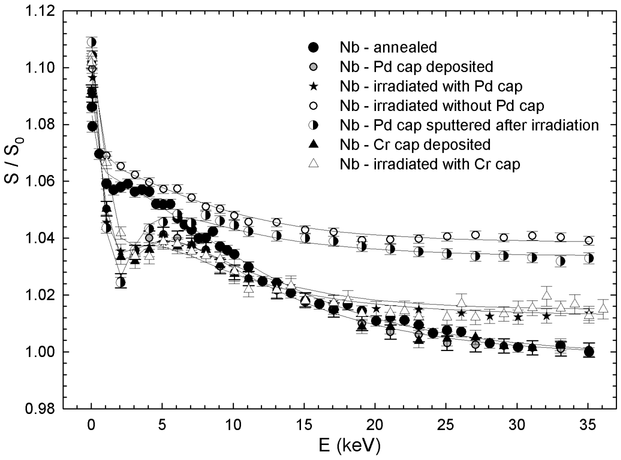

Fig. 1. The $S(E)$ curves measured by SPIS. The solid lines are fits by VEPFIT software.

3.2. Irradiation-induced defects

LT spectra of the irradiated Nb specimens can be fitted by two components. Lifetime of the longer component coming from positrons trapped at defects is plotted in Fig. 2 and lies around 190 ps, i.e. it is remarkably shorter than the Nb-vacancy lifetime $\tau_v = 222$ ps. As was already explained in Sect. 1, a shortening of the positron lifetime is caused by H atoms attached to vacancies. From the calculations it was found that an H atom is located not in the center of a vacancy, but on a line between the vacancy and the nearest neighbor octahedral interstitial position at a distance of ≈ 1.2 Å away from the center of the vacancy [5]. There are six such positions (crystallographically equivalent) around a vacancy. Figure 2 shows the calculated lifetime of trapped positrons as a function of the number of H atoms surrounding a vacancy. This lifetime decreases monotonically from τ_v down to τ_B with increasing number of H atoms. The lifetimes of trapped positrons measured on the irradiated specimens fall somewhere between that for a vacancy–hydrogen (v–H) pair and for a vacancy surrounded by two hydrogen atoms (v–2H). This result suggests that vacancies created by electron irradiation are surrounded by one or two H atoms. In order to separate these two contributions, the LT spectra were decomposed into three components with fixed lifetimes $\tau_3 = 204$ ps (v–H) and $\tau_2 = 182$ ps (v–2H). Results of this decomposition are shown in Table.

The concentrations $c_{\mathrm{v-H}}$ and $c_{\mathrm{v-2H}}$ of v–H and v–2H complexes were calculated using the three-component simple trapping model [4]:

$$c_{\mathrm{v-H}} = \frac{I_2}{\nu}\left(\frac{\tau_2 - \tau_1}{\tau_1 \tau_2}\right), \tag{1}$$

$$c_{\mathrm{v-2H}} = \frac{I_3}{\nu}\left(\frac{\tau_3 - \tau_1}{\tau_1 \tau_3}\right), \tag{2}$$

The specific trapping rate $\nu = 1 \times 10^{14}\ \mathrm{s}^{-1}$ [4] was used both for v–H and v–2H.

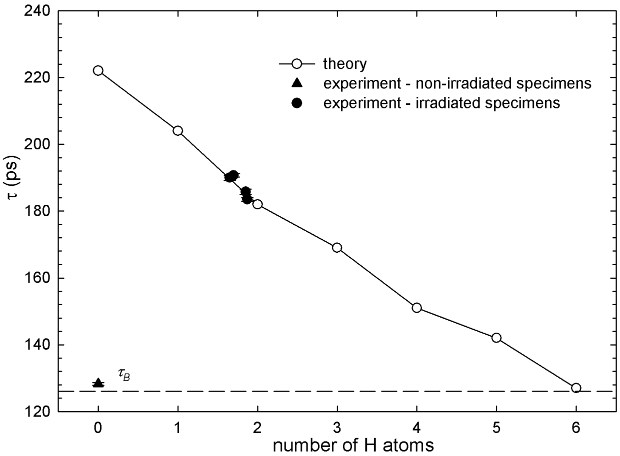

Fig. 2. Calculated lifetime of positrons trapped at Nb-vacancy surrounded by various numbers of H atoms (open circles), experimental lifetimes measured on non-irradiated specimens (full triangle) and irradiated samples (full circles). The mean number of H atoms surrounding vacancies in the irradiated specimens was calculated as $(c_{\mathrm{v-H}} + 2c_{\mathrm{v-2H}})/(c_{\mathrm{v-H}} + c_{\mathrm{v-2H}})$.

It is expected that ν for v–2H is slightly shorter than that for v–H, but this small difference was neglected in the present approach. The obtained results collected in Table revealed that the v–2H complexes are the dominating type of defects in all irradiated specimens. H was introduced into the irradiated specimens most probably from water vapor molecules present constantly in air which were ionized by the irradiation electrons. Moreover, the bombarding electrons break (at least partially) a thin oxide layer on the top of Nb which normally represents a barrier for H uptake. Hence, our results fully support the conclusions given in Refs. [6, 7].

The $S(E)$ curves measured by SPIS on the irradiated specimens are plotted in Fig. 1. A drop of S at low energies is due to positron annihilations inside the Pd cap. At higher positron energies S always converges towards the bulk value. The $S(E)$ curves were fitted by VEPFIT and the obtained results are shown in Table. In general, the irradiated specimens exhibit a higher S parameter and shorter positron diffusion length due to vacancy-hydrogen complexes created by irradiation. The net concentration of the irradiation-induced defects $c_{\mathrm{D}} = c_{\mathrm{v-H}} + c_{\mathrm{v-2H}}$ was calculated from the equation

$$c_{\mathrm{D}} = \frac{1}{\nu\tau_{\mathrm{B}}}\left(\frac{L_{+,\mathrm{B}}^2}{L_+^2} - 1\right), \tag{3}$$

with L_+ being the positron diffusion length in the irradiated specimen. One can see in Table that there is a reasonable agreement between the net concentration of defects c_{D} obtained from SPIS data and $c_{\mathrm{v-H}} + c_{\mathrm{v-2H}}$ determined by LT spectroscopy.

Taking into account a high mobility of hydrogen in Nb even at room temperature [2], and a positive binding energy ≈ 0.5 eV of v–H complex [5], it is reasonable to assume that virtually all H atoms in the Nb specimens are trapped at the irradiation-induced vacancies. Hence, the H concentration c_{H} in the irradiated specimens can be estimated from a simple equation

$$c_{\mathrm{H}} = c_{\mathrm{v-H}} + 2c_{\mathrm{v-2H}} \tag{4}$$

and is given in Table. All irradiated specimens contain a very similar amount of H. A slightly lower c_{H} value found in the specimen irradiated with a Pd cap is most probably only a statistical fluctuation.

3.3. Influence of Pd and Cr over-layer

Figure 1 shows $S(E)$ curve for the specimen with a Pd cap deposited after irradiation. Clearly the vacancy–hydrogen complexes remain practically unchanged after sputtering of the Pd cap on the irradiated specimen surface. On the other hand, the specimens with Pd cap deposited *prior* to irradiation (i.e. irradiated with Pd cap) exhibit a higher relative fraction of v–2H complexes, see Table. The same conclusion can be drawn for the specimen irradiated with Cr cap. From the results collected in Table it can be deduced that v–2H complexes represent $\approx 85\%$ of defects in the specimens irradiated with Pd (or Cr) cap, while in the specimens irradiated without Pd cap it is only 65–70%. This difference is due to a catalytic effect of the Pd over-layer, which enhances hydrogen uptake into Nb [15]. A thin Pd layer with its lower desorption energy compared to Nb prevents preferential occupation of subsurface sites over bulk sites, but keeps the surface relatively clean and with enough sites for dissociation of incoming hydrogen molecules [15]. Cr exhibits also a lower desorption energy than Nb [16]. Thus, a thin Cr over-layer is expected to enhance the hydrogen uptake in a similar manner as a Pd cap. Hence, the irradiation-induced vacancies in specimens irradiated with Pd (or Cr) cap are on average surrounded by more H atoms.

The net concentration of irradiation-induced defects in the specimens irradiated with Pd (or Cr cap) seems to be slightly lower than in the specimens irradiated without Pd cap. This effect cannot be explained by a dependence of the reflection coefficient of bombarding electrons on the Z value of the material deposited on the surface. Pd exhibits $Z_{\mathrm{Pd}} = 46$ (i.e. higher than $Z_{\mathrm{Nb}} = 41$), but $Z_{\mathrm{Cr}} = 24$ is lower. Thus, slightly lower c_{D} values found in the specimens irradiated with Pd (or Cr) are most probably due to a slightly lower specific trapping rate of v–2H complexes compared to v–H complexes.

4. Conclusions

Nb specimens irradiated by 10 MeV electrons were investigated in this work. It was found that vacancies introduced into Nb by electron irradiation are surrounded by H atoms. The irradiated Nb specimens contain a mixture of v–H and v–2H complexes. The v–2H complexes represent a predominant type of defects in all irradiated specimens. The specimens irradiated with Pd (or Cr) cap contain a higher relative fraction of v–2H complexes.

5. Acknowledgments

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