*Materials Science Forum Vols. 445-446 (2004) pp. 60-62*
*online at http://www.scientific.net*

# Hydrogen-Induced Defects in Niobium Studied by Positron Annihilation

J. Čížek[1], I. Procházka[1], R. Kužel[1], F. Bečvář[1], M. Cieslar[1], G. Brauer[2], W. Anwand[2], R. Kirchheim[3], A. Pundt[3]

[1] Faculty of Mathematics and Physics, Charles University Prague,
V Holešovičkách 2, CZ-18000 Praha 8, Czech Republic, jcizek@mbox.troja.mff.cuni.cz

[2] Institut für Ionenstrahlphysik und Materialforschung, Forschungszentrum Rossendorf,
Postfach 510119, D-01314, Dresden, Germany

[3] Institut für Materialphysik, Universität Göttingen,
Tammannstrasse 1, D-37073, Göttingen, Germany

**Keywords:** hydrogen, niobium, vacancy.

**Abstract.** Changes of the defect structure of niobium induced by hydrogen loading are presented in this work. It was found that annealing of virgin bulk Nb (99.9%) at 1000 °C for 1h leads to a complete recovery of defects. Subsequently, the defect-free samples were step-by-step electrochemically loaded with hydrogen up to $x_H = 0.06$ [H/Nb atom ratio], i.e. in the α-phase region, where the Nb-H system represents a single-phase solid solution. The evolution of the microstructure with increasing hydrogen concentration was studied by X-ray diffraction and two complementary techniques of positron annihilation spectroscopy (PAS), namely positron lifetime spectroscopy and slow positron implantation spectroscopy with measurement of Doppler broadening. It was found that new defects were created due to hydrogen loading. The concentration of these hydrogen-induced defects increases with increasing hydrogen concentration. A comparison of PAS results with theoretical calculations revealed that complexes consisting of a vacancy, surrounded likely by four hydrogen atoms, were introduced into the samples due to hydrogen loading.

## Introduction

Hydrogen storage in metals is of considerable importance for practical applications. Therefore, the hydrogen behavior in metals has been studied for many years. Hydrogen atoms exhibit a high mobility in metals at room temperature. As a consequence, hydrogen interaction with lattice defects usually plays an important role. Besides hydrogen trapping at existing open-volume defects, hydrogen loading can also create new defects. Recently, Shirai et al. [1] observed a huge increase of the defect density in a hydrogenated $LaNi_5$ alloy. In order to clarify the nature of hydrogen-induced defects in metals, we studied bulk Nb with various amounts of hydrogen. The investigations were performed by means of positron annihilation spectroscopy (PAS) and X-ray diffraction (XRD) at low hydrogen concentrations where the Nb-H system represents a *single-phase* solid solution (α-phase). It excludes the possibility of defect creation by precipitation of hydrides.

## Experimental Details

Virgin bulk Nb (99.9%) samples were firstly annealed at 1000 °C for 1 h to anneal out all existing defects. Subsequently, the surface of the samples was covered with a 30 nm thick Pd cup in order to prevent them from oxidation and to facilitate hydrogen absorption. The samples were step- by-step loaded with hydrogen by electrochemical charging, see [2,3] for details. Defect studies were performed by positron lifetime (PL) measurement using a fast-fast PL spectrometer [4] and slow

---

The extended stays of Jakub Čížek at Forschungszentrum Rossendorf and University Göttingen were financially supported by The Alexander von Humboldt Foundation and the project COST OC.523.50.

positron implantation spectroscopy (SPIS) on the magnetically guided system "SPONSOR" [5]. Lattice expansion was measured by XRD using Cu-$K_\alpha$ radiation.

## Results and Discussion

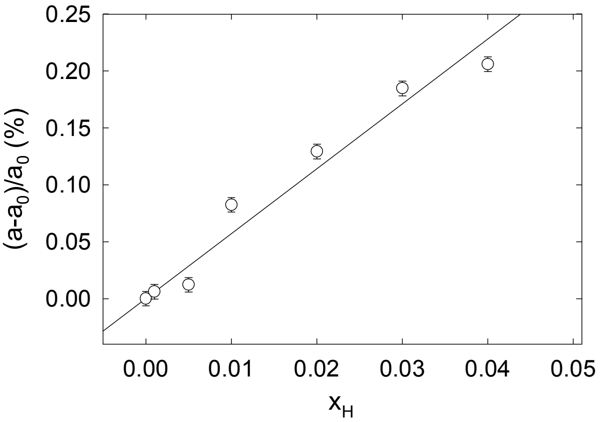

Fig. 1 Relative lattice expansion as a function of hydrogen concentration $x_H$.

The XRD spectra of the sample loaded in the α-phase region exhibit peaks corresponding to Nb reflections. The lattice parameter a was determined as a function of hydrogen concentration $x_H$ [H/Nb atom ratio]. As expected for the α-phase [6], the relative lattice expansion (see Fig. 1) is linearly proportional to $x_H$, i.e. $(a-a_0)/a_0 = \xi\, x_H$, where $a_0$ denotes the lattice parameter for the virgin sample. From a linear fit of the experimental data we obtained $\xi = 0.058 \pm 0.004$ in excellent agreement with the literature [6]. The virgin sample can be considered as defect-free because it exhibits a single component PL spectrum with lifetime $\tau_B = 128.3 \pm 0.4$ ps, which agrees well with reported bulk Nb lifetimes [7]. The lifetimes of exponential components found in PL spectra of hydrogen loaded samples are shown in Fig. 2A) as a function of $x_H$. A new component with a lifetime $\tau_2 \approx 150$ ps appeared in the PL spectra of hydrogen-loaded samples. This component arises from positrons trapped at defects created by hydrogen loading. One can see in Fig. 2B) that the relative intensity $I_2$ of this component increases with $x_H$. In order to clarify the physical nature of the hydrogen-induced defects observed in our samples, we compared $\tau_2$ with the lifetime $\tau_v$ of positrons trapped in Nb-monovacancies. We measured $\tau_v = 210 \pm 10$ ps on a reference Nb sample after its rapid quenching from 1000 $^o$C into water of room temperature. This value is in reasonable agreement with theoretical calculations, which revealed $\tau_v = 222$ ps [2]. Clearly, the observed lifetime $\tau_2$ (~ 150 ps) of positrons trapped at hydrogen-induced defects is substantially lower than the lifetime of positrons trapped at Nb-vacancies. Furthermore, the hydrogen-induced volume expansion in the α-phase concentration range is a reversible elastic process and no plastic deformation of the sample takes place. Therefore, the creation of dislocations in the hydrogen-loaded samples is not expected. This was confirmed by direct transmission electron microscopy observations. Taking into account an attractive interaction of H and a vacancy, a natural explanation is then that the hydrogen-induced defects represent vacancies associated with one or more hydrogen atoms. The presence of a hydrogen atom bound to a vacancy results in an increase of the local electron density, which is reflected by a decrease of the lifetime of a trapped positron. To study this effect quantitatively, the

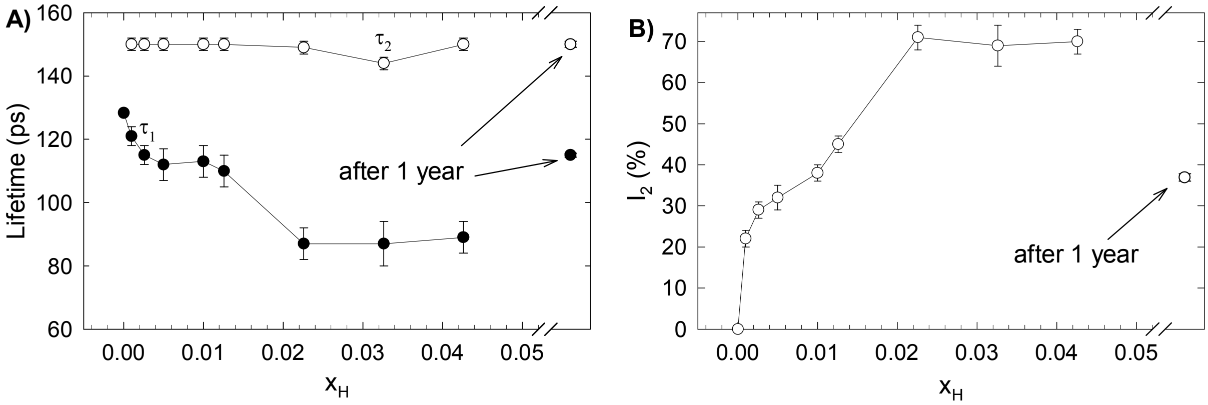

Fig. 2 A) The dependence of positron lifetimes on hydrogen concentration, B) the relative intensity $I_2$ of the hydrogen-induced defect component as a function of hydrogen concentration.

lifetimes of trapped positrons were calculated as a function of the number of hydrogen atoms bound to a vacancy. A detailed description of the calculations can be found in [2]. The results shown in Fig. 3A) revealed that the lifetime of trapped positrons remarkably decreases with an increasing number of hydrogen atoms associated to the vacancy. The lifetime of about 150 ps observed in our experiments corresponds to a vacancy surrounded by four hydrogen atoms. The S-E curves obtained by SPIS are plotted in Fig 3B) for samples loaded up to various $x_H$. A plateau of S at high energies, which corresponds to a situation when practically all positrons annihilate in bulk Nb, remarkably increases with $x_H$. It directly indicates an increase of the defect density in the bulk due to hydrogen loading. Note that a local minimum of S at low energies is due to positron annihilation inside the Pd cup. This minimum is absent in the virgin sample because it was measured prior to the Pd cup sputtering. Thus, one can conclude that the SPIS results confirm the creation of hydrogen-induced defects in concordance with PL measurements. Moreover, SPIS indicates that it is not a surface effect but it takes place in the bulk of the studied samples. The sample loaded up to $x_H = 0.043$ was left for one year on air. Fig. 2 B) shows that it resulted in a decrease of $I_2$ roughly to half of its value measured immediately after loading. Obviously, the decrease of the defect density is due to a release of hydrogen from the sample with ageing at room temperature. Hence, the existence of hydrogen-induced defects seems to be conditioned by the presence of hydrogen inside the sample. It is therefore possible that the introduction of these defects is a reversible process, and a complete removal of hydrogen may result also in a complete disappearance of the hydrogen-induced defects.

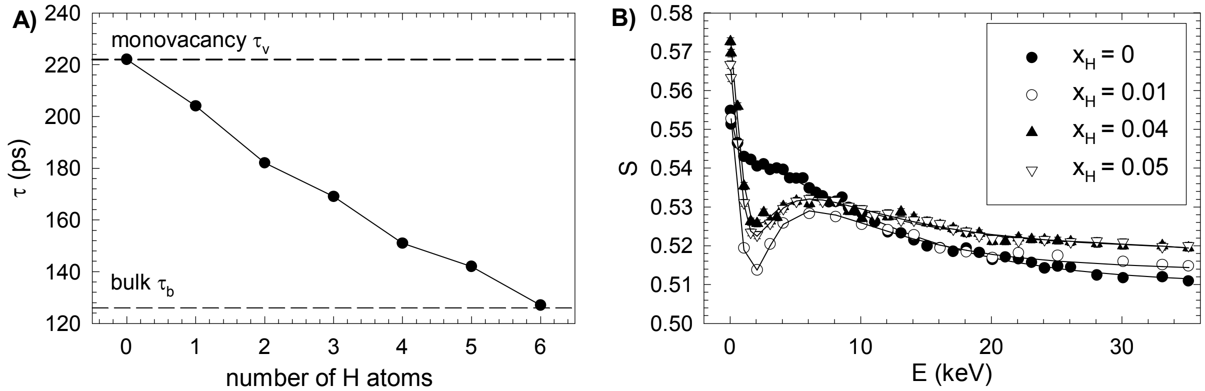

Fig. 3 A) Calculated lifetime of positrons trapped in a vacancy as a function of the number of surrounding hydrogen atoms, B) S-E curves for a sample with various amount of hydrogen.

## Conclusions

A defect-free bulk Nb was step-by-step electrochemically loaded with hydrogen in the α-phase region. New defects were created in the bulk due to hydrogen loading and their concentration increases with hydrogen amount. From a comparison with theoretical calculations it turned out that the hydrogen-induced defects are most probably vacancies surrounded by four hydrogen atoms.

## References

[1] Y. Shirai, H. Araki, T. Mori, W. Nakamura, K. Sakaki, J. Alloys Comp. 330 (2002), p. 125.

[2] J. Čížek, I. Procházka, F. Bečvář, R. Kužel, M. Cieslar, G. Brauer, W. Anwand, R. Kirchheim, A. Pundt, submitted to Phys. Rev. B (2003).

[3] R. Kircheim, Prog. Mat. Sci. 32 (1988), p. 261.

[4] F. Bečvář, J. Čížek, L. Lešťák, I. Novotný, I. Procházka, F. Šebesta, Nucl. Instr. Meth. A 443, (2000), p. 557.

[5] W. Anwand, H.-R. Kissener, G. Brauer, Acta Physica Polonica A 88 (1995), p. 7.

[6] H. Peisl, in: Hydrogen in Metals I, eds. G. Alefeld, J. Völkl, Springer-Verlag, Berlin 1978, p. 53.

[7] P. Sterne, J. Pask, B. Klein, Appl. Surf. Sci. 149 (1999), p. 238.