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Hydrogen-induced defects in niobium studied by positron annihilation spectroscopy

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Abstract

Changes of the defect structure of Nb induced by hydrogen loading were studied by positron annihilation spectroscopy (PAS). Two sets of samples with different initial microstructure were studied: (i) well-annealed bulk samples, and (ii) thin nanocrystalline films. First, the microstructure of the virgin samples was characterized. Subsequently, the samples were step-by-step electrochemically loaded with hydrogen in the α-phase region, where the Nb–H system represents a single-phase solid solution. Two complementary PAS techniques, namely positron lifetime (PL) spectroscopy and slow positron implantation spectroscopy (SPIS), and in addition X-ray diffraction were applied to investigate the evolution of the microstructure with increasing hydrogen concentration. It was found that new defects were created in the bulk Nb sample due to hydrogen loading. Their concentration 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 are formed. Hydrogen trapping in open-volume defects at grain boundaries was observed in the thin Nb films.

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1. Introduction

The behavior of hydrogen in a metal host lattice can be significantly influenced by interaction with lattice defects. It is well known that hydrogen can be trapped at vacancies [1] and dislocations [2]. Moreover, hydrogen is not only trapped at existing open-volume defects, but new defects can also be created by hydrogen loading [3]. However, the nature of the hydrogen-induced defects and the mechanism of their creation are still not completely understood. Similarly to hydrogen, a positron is a very small probe with high mobility in a host metal lattice thereby having a strong attractive interaction with open-volume defects, which represent positron traps. The positron annihilation rate is given by an overlap of positron and electron wave functions. Hence, the lifetime of a trapped positron depends on the local electron density at the corresponding defect. Positron lifetime (PL) spectroscopy [4] is based on the measurement of positron lifetimes in a material of interest. Any measured PL spectrum represents a histogram of actual lifetimes of several millions of positrons. Usually, it can be described as a sum of a few exponential components smeared by the resolution function of the spectrometer. Lifetimes of the exponential components allow for identification of defect types present in the studied specimen. Relative intensities of the components are related to defect

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densities. The Doppler broadening (DB) of the annihilation gamma rays represents another observable related to the positron annihilation process. The DB is almost completely determined by the momentum of the annihilating electron because the kinetic energy of the thermalized positron is only about 0.025 eV. Thus, the DB mainly carries information about the electron momentum distribution. The DB is quantified by so-called line-shape parameters. The *S* parameter used in the present work is a ratio of the central peak region to the net peak area and characterizes mainly contribution of positron annihilations with the low-momentum electrons. The positron annihilation techniques are non-destructive and exhibit a high sensitivity to open-volume defects, see [4] for more details. It makes them an ideal tool for the investigation of hydrogen-defect interactions as well as the characterization of hydrogen-induced defects. In the present work, defect studies of hydrogen loaded Nb were performed to clarify the nature of hydrogen-induced defects and to characterize influence of defects on the hydrogen behavior.

2. Experimental details

Bulk Nb (99.9%) samples were firstly annealed at 1000 °C for 1 h to remove defects introduced by plastic deformation during casting and shaping. Nanocrystalline Nb films with a thickness of about 1.5 μm on Si substrate were prepared using magnetron DC sputtering at room temperature. The surface of all samples was covered with a 30 nm thick Pd cap in order to prevent oxidation and to facilitate hydrogen absorption. The samples were step-by-step loaded with hydrogen by electrochemical charging [2]. Defect studies were performed by PL measurements using a fast-fast PL spectrometer with timing resolution of 160 ps [5] and by slow positron implantation spectroscopy (SPIS) with DB measurements at a magnetically guided positron beam “SPONSOR” [6]. Lattice expansion was measured by X-ray diffraction (XRD) using Cu Kα radiation.

3. Results and discussion

The bulk Nb sample exhibits a single component PL spectrum with lifetime $\tau_1 = 128.3(4)$ ps, which is in good agreement with calculated Nb bulk positron lifetime [7]. Hence, the annealing at 1000 °C lead to a complete recovery of defects and the virgin bulk sample can be considered as a defect-free material. The lattice constant $a_0 = 3.3029(3)$ Å determined by XRD agrees well with the value given in PDF-2 database [8]. The lattice constant a increases with hydrogen concentration. Dependence of the relative lattice expansion $(a - a_0)/a_0$ on hydrogen concentration x_H (H/Nb ratio) is plotted in Fig. 1a. As expected for the α-phase region it is directly proportional to x_H, i.e. $(a - a_0)/a_0 = \xi x_\mathrm{H}$. The coefficient $\xi = 0.058(4)$ determined from the data shown in Fig. 1a is in excellent agreement with the literature [9].

The Nb film is clamped at an elastically hard substrate, which prevents in-plane expansion and leads to a larger expansion out-of-plane. An increase of a at a direction tilted 60° with respect to the normal to the film surface was measured besides the out-of-plane expansion, see Fig. 1a. A significant difference of film expansion in these two directions confirms the picture that the in-plane expansion of the film is prevented.

A new component with a lifetime $\tau_2 \approx 150$ ps appeared in the PL spectrum of the hydrogen loaded bulk Nb sample. It directly indicates the formation of new defects created by hydrogen loading. The lifetime τ_2 remains constant with increasing amount of hydrogen. On the other hand, the relative intensity I_2 of this component shown in Fig. 1b significantly increases with x_H. It means that the nature of the hydrogen-induced defects does not change, while their concentration goes up with x_H. The lifetime τ_2 is remarkably lower than the lifetime $\tau_v = 220(10)$ ps of positrons trapped at Nb vacancies [7]. Thus, it may be concluded that the free volume of the hydrogen-induced defect is lower than that of a monovacancy in Nb.

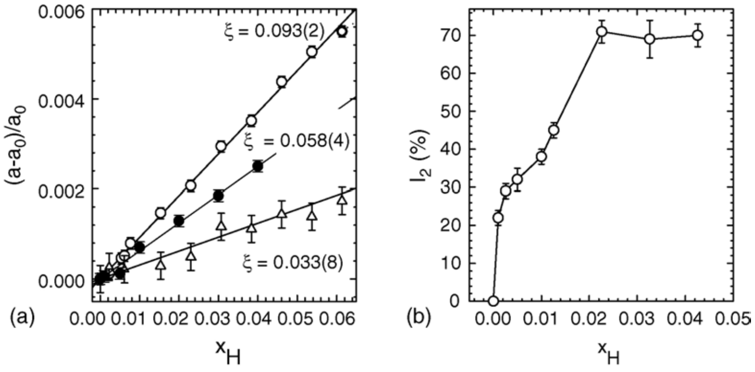

Fig. 1. (a) The relative lattice expansion $(a - a_o)/a_o$ as a function of hydrogen concentration. Results for bulk Nb are plotted by full circles. In case of Nb film the relative lattice expansion out of plane (open circles) and in direction of 60° with respect to normal to the film surface (open triangles) are compared. (b) Dependence of relative intensity I_2 of positrons trapped at hydrogen-induced defects on x_H.

The hydrogen-induced volume expansion in the α-phase concentration range is a reversible elastic process, and no plastic deformation takes place. Therefore, the creation of dislocations is not expected. Indeed, no dislocations could be observed in the hydrogen loaded bulk Nb sample by transmission electron microscopy. Taking into account an attractive interaction of hydrogen atom and a vacancy, a natural explanation of the observed effect is that vacancies associated with one or more hydrogen atoms are created. 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 lifetime of trapped positrons. This effect was confirmed by theoretical calculations [7] which revealed that the lifetime of trapped positrons monotonically decreases with increasing number of hydrogen atoms surrounding the vacancy. The lifetime of 150 ps observed in experiment corresponds to a vacancy surrounded by four hydrogen atoms. Thus, we conclude that complexes of vacancies surrounded with four hydrogen atoms were formed by hydrogen loading in the bulk Nb sample. The binding energy $E_{\mathrm{B}} = 0.50$ eV of a hydrogen atom to a vacancy in Nb was calculated using the effective medium theory [7]. The vacancy formation energy in Nb $E_{\mathrm{f}} = 2.32$ eV [11] is reduced due to presence of diluted interstitial hydrogen. An order-of-magnitude estimation (neglecting the hydrogen-hydrogen interaction) of the formation energy for vacancy surrounded by 4 hydrogen atoms yields $E_{\mathrm{f}} - 4E_{\mathrm{B}} = 0.32$ eV. The equilibrium concentration of vacancies associated with 4 hydrogen atoms (see [7] for details) can be estimated using equation $c \approx \exp(S_{\mathrm{f}}/k)\exp[-(E_{\mathrm{f}} - 4E_{\mathrm{B}})/kT]$, where $S_{\mathrm{f}} = (2 - 3)$ k is known to hold for most of metals [12]. For the equilibrium concentration of vacancy—4H complexes at room temperature we obtain $c \approx (2\text{–}6) \times 10^{-5}$ at.$^{-1}$. The concentration of vacancy—4H complexes calculated from PL results using the two-state trapping model [4] at hydrogen concentration $x_{\mathrm{H}} = 0.04$ amounts $c \approx 3 \times 10^{-5}$ at.$^{-1}$. Note that the specific positron trapping rate 1×10^{14} s^{-1} was used [7]. Thus, we can conclude that there is a reasonable agreement between the estimated equilibrium concentration of vacancy—4H complexes and the measured concentration of hydrogen-induced defects. It indicates that formation of hydrogen-induced defects in the α-phase could be explained by lowering of the vacancy formation energy due to presence of hydrogen. The dependence of S parameter on positron energy E for a virgin Nb film is shown in Fig. 2a. The initial drop of S at low energies is due to positron annihilations inside the Pd cap. The fraction of positrons annihilating in the Nb layer increases with increasing energy. It is reflected by an increase of S. From $E > 4$ keV almost all positrons annihilate in the Nb layer which is reflected in a plateau-like behavior of the S–E dependence. At $E > 25$ keV positrons penetrate into the Si substrate. It leads to a further increase of S. The S value characterizing the Nb layer lies well above $S = 0.5095(3)$ representing defect free Nb bulk. It directly indicates the presence of a high concentration of defects in the film. We expect that the majority of positrons annihilates from a trapped state in open-volume defects at grain boundaries (GB's) because of small grain size (<100 nm), which leads to a high volume fraction of GB's. Similarly to positrons, hydrogen can be trapped in open volume defects at GB's as well. The presence of hydrogen atoms at the vicinity of the defects reduces the open volume and increases the local density of core electrons with higher momentum. It results in a shortening of the positron lifetime, and a decrease of the S parameter characterizing the Nb layer, S_{Nb}. A significant decrease of S_{Nb} with increasing x_{H} can be seen in selected S–E curves in Fig. 2a. The dependence of S_{Nb} on x_{H} obtained from fit using the analyzing software code VEPFIT [10] is plotted in Fig. 2b. From the beginning of hydrogen loading it is thought that hydrogen firstly fills the open volumes (deep traps) at GB's, which is reflected by a radical decrease of S_{Nb}. Subsequently, for $x_{\mathrm{H}} \geq 0.03$ the deep traps are filled and S_{Nb} does not change anymore. Note that formation of new defects (e.g. vacancy-H complexes or dislocations) would result in an increase S_{Nb} due to increasing fraction of trapped positrons. Thus, we can conclude that contrary to the bulk sample, no formation of hydrogen-induced defects occurred in the Nb film loaded up to $x_{\mathrm{H}} = 0.17$. This is most probably due to a high density of open volume defects (hydrogen traps), existing already in the virgin film, i.e. before the loading.

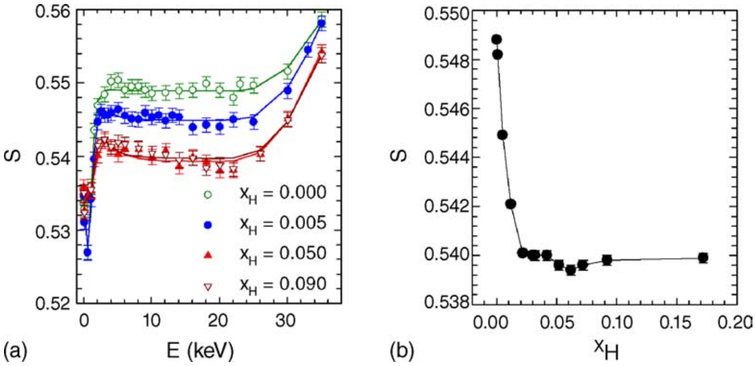

Fig. 2. Results obtained at hydrogen loaded Nb films: (a) selected S–E curves for various hydrogen concentrations x_{H}, the solid lines represent a fit by VEPFIT. (b) Dependence of the S parameter for Nb layer (S_{Nb}) on x_{H}.

4. Conclusions

Vacancies associated with four hydrogen atoms are formed by hydrogen loading in bulk Nb. The concentration of these hydrogen-induced defects increases with increasing hydrogen concentration. In a nanocrystalline Nb film, hydrogen trapping in open-volume defects at grain boundaries is observed but no formation of hydrogen-induced defects occurs at hydrogen concentrations $x_H \leq 0.17$.

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