ARTICLE IN PRESS

Journal of Alloys and Compounds xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Hydrogen-induced defects and multiplication of dislocations in Palladium

J. Čížek *, O. Melikhova, I. Procházka

Charles University in Prague, Faculty of Mathematics and Physics, V Holešovičkách 2, CZ-180 00 Praha 8, Czech Republic

ARTICLE INFO

Article history:
Available online xxxx

Keywords:
Palladium
Hydrogen
Defects
Positron annihilation
Hardness

ABSTRACT

In the present work positron lifetime spectroscopy was employed for investigation of hydrogen-induced defects in Pd. Well annealed polycrystalline Pd samples were electrochemically charged with hydrogen and the development of defects with increasing hydrogen concentration was investigated. At low concentrations (α-phase region, $x_H < 0.017$ H/Pd) hydrogen loading introduced vacancies surrounded by hydrogen atoms and characterized by a positron lifetime of ≈200 ps. When the hydrogen concentration exceeded 0.017 H/Pd the α-phase transformed into the hydrogen rich α′-phase. This generated dislocations characterized by a positron lifetime of ≈170 ps. Dislocations can accommodate a large volume mismatch between the α and the α′-phase. Hardness testing revealed that absorbed hydrogen made Pd harder. In the α-phase region hardness increased due to solid solution hardening caused by dissolved hydrogen. Dislocations created by the α to α′-phase transition caused strain hardening which led to an additional increase of hardness.

1. Introduction

Palladium (Pd) is able to absorb relatively large amount of hydrogen and can be charged with hydrogen easily [1]. This makes Pd–H an ideal model system for investigation of hydrogen absorption, diffusion and interaction with defects in the metal lattice. Hydrogen occupies octahedral interstitial sites in the fcc Pd lattice and causes lattice expansion. Above the critical temperature of ≈295 °C hydrogen is fully soluble in Pd up to the atomic ratio of 1.0 H/Pd [1]. At lower temperatures there is a miscibility gap where the Pd–H system consists of a mechanical mixture of two phases: the α-phase with lower hydrogen content and the hydrogen-rich α′-phase [2]. Both these phases exhibit fcc structure and differ by the hydrogen content only, i.e. by the average number of octahedral sites occupied by hydrogen [1]. The lattice parameters of the α and the α′-phase are incommensurable and their volume misfit is as high as 10% [1]. At ambient temperature the miscibility gap extends from the hydrogen concentration 0.017 H/Pd up to 0.58 H/Pd [2].

It has been reported that lattice defects are introduced into Pd by hydrogen loading. In particular Fukai and Ōkuma [3] observed extraordinary high vacancy concentration in a Pd annealed at a high hydrogen pressure of 5 GPa. Cheng et al. [4] found that the dislocation density in a cold rolled Pd–H is remarkably enhanced compared to a pure Pd subjected to the same deformation. The enhancement of the defect density in Pd containing hydrogen can be understood in the terms of reduction of the defect formation energies by segregating hydrogen proposed by Kirchheim [5].

The hydrogen-induced defects were usually characterized indirectly by X-ray diffraction measurements of the lattice contraction for vacancies [3] or by the line shape analysis of X-ray diffraction profiles in the case of dislocations [4]. Positron lifetime (LT) spectroscopy [6] is a unique non-destructive technique which enables direct probing of open volume defects on the atomic scale. In the present work LT spectroscopy was employed for characterization of hydrogen-induced defects in Pd. The LT defect studies were combined with hardness testing to monitor changes of mechanical properties of Pd loaded with hydrogen.

2. Experimental

Polycrystalline Pd (99.95% purity) specimens with dimensions 10 × 10 × 0.25 mm^3 were firstly annealed at 1000 °C for 2 h in a vacuum to remove virtually all defects introduced during previous casting and shaping. Subsequently the specimens were step-by-step electrochemically charged with hydrogen in a cell filled with electrolyte consisting of a mixture of H_3PO_4 and glycerine (volume ratio 1:2). Hydrogen loading was performed at ambient temperature using a galvanostat and applying constant current pulses between a Pt counter electrode (anode) and the Pd sample (cathode). The current density on the sample was kept at 0.3 mA/cm^2. The hydrogen concentration introduced into the sample was calculated from the transported charge using the Faraday's law. Hydrogen is very mobile in the

---

* Corresponding author. Tel.: +420 221912788.
E-mail address: jakub.cizek@mff.cuni.cz (J. Čížek).

http://dx.doi.org/10.1016/j.jallcom.2014.12.155

Please cite this article in press as: J. Čížek et al., J. Alloys Comp. (2015), http://dx.doi.org/10.1016/j.jallcom.2014.12.155

Pd lattice even at room temperature. The room temperature hydrogen diffusion coefficient in Pd is 4×10^{-11} m^2 s^{-1} [7]. Hence, the mean hydrogen diffusion length in Pd during the period of 1 h is as high as ≈0.4 mm. Since the electrochemical charging of the samples took several hours one can expect that the hydrogen concentration equilibrates by diffusion and becomes uniform across the whole sample.

A digital positron lifetime (LT) spectrometer [8] with excellent time resolution of 145 ps (FWHM of the resolution function) was employed for LT investigations. At least 10^7 positron annihilation events were accumulated in each LT spectrum which was subsequently decomposed into individual components using a maximum likelihood procedure [9]. A $^{22}Na_2CO_3$ positron source (~1.5 MBq) deposited on a 2 μm thick Mylar foil was always forming a sandwich with two identically treated Pd specimens. The source contribution in the LT spectra was determined using a well annealed Pd sample. It consisted of two components with the lifetimes of ≈368 ps and ≈1.5 ns, and the corresponding intensities of ≈8% and ≈1% which come from positrons annihilated in the Na_2CO_3 source spot and the covering Mylar foil, respectively. The source components were always subtracted from the LT spectra.

A Struers Durascan 2 hardness tester was used for the Vickers hardness (HV) measurements. Hardness of hydrogen loaded samples was measured using the load of 0.5 kg applied for 10 s.

3. Results and discussions

The annealed Pd sample exhibits a single component LT spectrum with the lifetime $\tau_B = (110.1 \pm 0.5)$ ps. This lifetime agrees well with the calculated bulk lifetime for Pd [10]. Hence, one can conclude that the defect density in the annealed sample is very low, below the sensitivity threshold of PAS. Virtually all positrons in the annealed Pd are annihilated in the free state, i.e. delocalized in the lattice and not trapped at defects.

The LT spectra of the Pd samples loaded with hydrogen can be well fitted by two exponential components. The dependence of the positron lifetimes τ_1, τ_2 resolved in the LT spectra on the hydrogen concentration x_H introduced into the sample is plotted in Fig. 1a. The shorter component with the lifetime $\tau_1 < \tau_B$ represents a contribution of free positrons delocalized in the lattice. Note that shortening of the lifetime τ_1 is due to positron trapping at defects as described by the simple trapping model [11]. The longer component with the lifetime τ_2 can be attributed to positrons trapped at defects since its lifetime is higher than τ_B. This component appeared in hydrogen-loaded sample already after the first loading step ($x_H = 0.005$ H/Pd). It means that these defects were created by hydrogen loading. The intensity I_2 of this component plotted in Fig. 1b grows with increasing hydrogen content in the sample. It testifies to increasing concentration of hydrogen-induced defects. In the α-phase region ($x_H < 0.017$ H/Pd) the lifetime τ_2 is approximately 200 ps. This value is close to the lifetime of 209 ps calculated for Pd vacancy using the self-consistent electron density and the generalized gradient approximation for the electron-positron correlation (LMTO-GGA approach) [10]. Hence, in the α-phase region hydrogen loading introduces vacancies. Slightly shorter value of $\tau_2 \approx 200$ ps measured in the experiment is likely due to hydrogen atoms bound to vacancies. Similar effect, i.e. shortening of positron lifetime due to hydrogen atoms attached to vacancy, was observed also in Nb loaded with hydrogen [12]. In Pd the shortening of the positron lifetime is smaller in magnitude compared to Nb indicating that hydrogen atoms are located farther away from the vacancy. Determination of the exact structure of the vacancy-hydrogen complexes in Pd requires *ab-inito* theoretical calculations which are out of the scope of this work. In the two-phase field ($x_H > 0.017$ H/Pd) the lifetime τ_2 gradually decreases down to ≈170 ps which is close to the lifetime of 160 ps reported for positrons trapped at dislocations in Pd [13]. Hence in the two-phase field hydrogen loading introduces not only vacancies but also dislocations. Since positrons trapped at both these defects contribute to the defect component the observed decrease of τ_2 is due to increasing population of dislocations.

To separate the contribution of positrons trapped at hydrogen-induced vacancies and dislocations the LT spectra were in further analysis decomposed into tree components: (i) the free positron component with the lifetime τ_1, (ii) the dislocation component with the lifetime τ_2 fixed at 160 ps and (iii) the vacancy component with the lifetime τ_3 fixed at 200 ps. Results of the three-component decomposition are presented in Fig. 2. The intensity I_3 of positrons trapped at vacancies rises sharply already in the α-phase field while the dislocation component with the intensity I_2 arises in the two-phase field only. Hence the α to α′-phase transition generates dislocations because dislocations allow for accommodation of the large volume misfit (≈10%) between the α and the α′-phase [14].

Fig. 3a shows the concentration of hydrogen-induced vacancies c_V calculated from the LT results using the three-state simple trapping model [15]

$$c_V = \frac{1}{\nu_V}\left[\frac{I_2 I_3}{I_1}\left(\frac{1}{\tau_3} - \frac{1}{\tau_2}\right) + \frac{I_3}{I_1}\left(\frac{1}{\tau_B} - \frac{1}{\tau_3}\right)\right], \tag{1}$$

where $\nu_V = 10^{14}$ s^{-1} is the specific positron trapping rate typical for vacancies in metals [15]. The density of dislocations ρ_D was calculated from the three-state trapping model as well

$$\rho_D = \frac{1}{\nu_D}\left[\frac{I_2 I_3}{I_1}\left(\frac{1}{\tau_2} - \frac{1}{\tau_3}\right) + \frac{I_2}{I_1}\left(\frac{1}{\tau_B} - \frac{1}{\tau_2}\right)\right] \tag{2}$$

using the specific trapping rate for dislocations $\nu_D = 0.5 \times 10^{-4}$ m^2 s^{-1} [15]. Fig. 3b shows the dislocation density plotted as a function of the hydrogen concentration in the sample.

From inspection of Fig. 3a it becomes clear that in the α-phase field hydrogen loading introduces vacancies and the concentration of hydrogen-induced vacancies increases up to ≈8 ppm measured

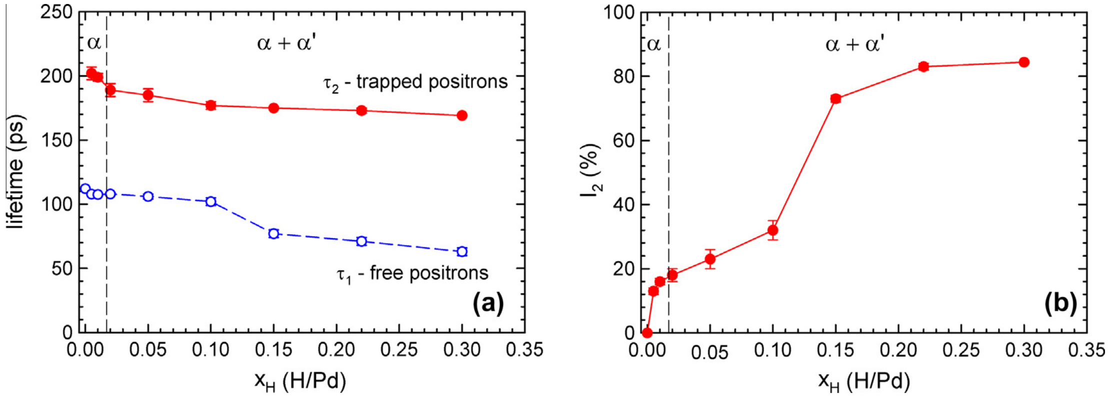

Fig. 1. Results of the two-component decomposition of LT spectra: positron lifetimes τ_1, τ_2 (a) and the intensity I_2 of positrons trapped at defects (b) plotted as a function of the hydrogen concentration x_H in the sample. Dashed line shows position of the phase boundary between the α-phase region and the two-phase field.

Please cite this article in press as: J. Čížek et al., J. Alloys Comp. (2015), http://dx.doi.org/10.1016/j.jallcom.2014.12.155