



Hydrogenation-induced microstructure changes in titanium



R. Laptev*, A. Lider, Yu. Bordulev, V. Kudiiarov, G. Garanin

Department of General Physics, Institute of Physics and Technology, National Research Tomsk Polytechnic University, Lenin Avenue 30, Tomsk 634050, Russia

ARTICLE INFO

Article history:

Available online 20 January 2015

Keywords:

Hydrogen
Defect complexes
Clusters
Positron annihilation
Doppler broadening
Positron lifetime

ABSTRACT

Microstructure changes of commercially pure titanium in a wide range of hydrogen concentrations from 0.8 at.% to 32.0 at.% were studied by means of positron lifetime spectroscopy and Doppler broadening spectroscopy. We have obtained new experimental data on the evolution of positron annihilation parameters τ_f , τ_d and their corresponding intensities I_f , I_d , as well as relative changes of parameters S/S_0 and W/W_0 depending on the hydrogen concentration in commercially pure titanium after gas-phase hydrogenation at 873 K. Results suggest that the hydrogenation of Ti samples up to concentrations of 1.31–2.27 at.% and subsequent cooling to a room temperature leads to the formation of vacancies and vacancy clusters. Further increase of the hydrogen concentration up to 32.0 at.% leads to the interaction of hydrogen with these defects and the formation of “cluster-hydrogen” and “vacancy-hydrogen” complexes.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The study of “metal-hydrogen” systems is interesting, in part, due to hydrogen’s diffusive mobility in metals and alloys, and its high reactivity, i.e., capability of forming complex systems. These complexes include vacancy-type defects, impurity atoms, dislocations, interstitial atoms and grain boundaries [1]. Moreover, hydrogen not only actively interacts with the existing structural defects [2,3]. It also induces formation of a large number of new defects [4–7]. The nature of hydrogen-induced defects and the mechanism of their formation are not yet fully understood.

Positron annihilation (PA) techniques are promising nuclear-physical methods for investigating structural defects in metal-hydrogen systems. The efficiency of PA methods for studying metal-hydrogen systems was demonstrated in [4,7–10]. Relevant issues that can be solved by these techniques include the study of the mechanisms and dynamics of the occurrence, transformation and disappearance of defects during hydrogenation.

In this context, the paper presents new experimental research on the defect structure evolution in commercially pure titanium after gas-phase hydrogenation and determination of the relationship between the annihilation parameters and characteristics of structural defects.

2. Experimental

Commercially pure titanium was chosen for this research, since this single-phase material is a widely used test material for the study of hydrogenation-induced defect formation [8]. Flat rectangular Ti samples with the dimensions of $30 \times 30 \times 1$ mm were prepared. The samples were cut from a sheet of titanium by spark cutting, mechanically polished and annealed in vacuum at 923 K for 1 h. The annealed samples were used in this research as a reference material.

Hydrogenation was performed by the Sieverts method using automatic Gas Reaction Controller LPB (Advanced Materials Corporation) [11] up to the specified concentrations in automatic mode at 873 K (with a heating rate of 4 K/min) and 67 kPa. Cooling was performed in vacuum at a rate of 1.5 K/min.

Phase composition and structural parameters of samples before and after the hydrogenation were studied using the XRD-6000 diffractometer with a $\text{Cu K}\alpha$ radiation source. Phase composition analysis was performed using the PCPDFWIN database and POWDER CELL 2.5 full profile analysis software.

Investigation of positron lifetime (PL) in the material and Doppler broadening (DB) shift of annihilation photons was performed using the equipment described in [9,10].

The samples were arranged in a so-called “sandwich configuration” (reference sample – positron source – hydrogenated sample), then packed in aluminum foil and mounted in a special sample-holder. PL and DB spectra were collected simultaneously. The positron source was represented by a ^{44}Ti isotope with an activity of 24.5 μCi .

Three PL spectra with 5×10^6 counts each were collected for every sample. Spectra were fitted using LT10 software [12]. The spectral analysis was performed implementing a multicomponent model.

DB spectra were acquired by collecting 2.5×10^5 counts and analyzed using SP software package [13]. The line-shape parameters S and W were also evaluated using the aforementioned software [14]. S parameter is ratio of central peak area to the entire area of Gaussian distribution; W parameter is ratio of Gaussian distribution side area to the entire area. Thus S parameter is associated with positron annihilation with valence electrons and W parameter with positron annihilation with core electrons. Relative values of these parameters (S/S_0 and W/W_0) were used for Doppler broadening analysis, where S_0 and W_0 are the shape parameters for reference samples, S and W are those for the samples after hydrogenation.

* Corresponding author.

E-mail addresses: laptevrs@tpu.ru (R. Laptev), liders@tpu.ru (A. Lider), bus@tpu.ru (Yu. Bordulev), kudiyarov@tpu.ru (V. Kudiiarov), garaningv@tpu.ru (G. Garanin).

Absolute hydrogen content in the samples was determined by melting in inert gas atmosphere using the RHEN602 analyzer (LECO Company).

3. Results and discussion

Positron lifetime spectra of reference samples without hydrogen were fitted by three exponential components. The first one corresponds to the positron lifetime in the bulk of the material. Lifetime values were determined for the two other components τ_a and τ_b , which refer to annihilation of the positrons trapped by Ti dislocations ($\tau_{\text{disl}} = 170$ ps) and monovacancies ($\tau_{\text{vac}} = 220$ ps [15]). The total intensity of these components did not exceed 1%. Thus after high temperature annealing at 923 K for 1 h, small amounts of dislocations and single vacancies could be identified. The average lifetime of positrons in the Ti-samples before hydrogenation was $\tau_{\text{avg}} = 143.1 \pm 0.4$ ps.

Figs. 1 and 2 show dependences of annihilation characteristics on the hydrogen content in titanium after gas-phase hydrogenation. Since the samples were hydrogenated up to concentrations varying from 0.9 at.% to 31.5 at.%, the hydrogen accumulation is not the only factor that affects the formation of defects. Another factor is a phase transformation process. Hydrogen concentrations corresponding to phase boundaries of the “titanium-hydrogen” system at 870 K for $\alpha/(\alpha + \beta)$ and $(\alpha + \beta)/\beta$ transitions are 7.58 at.% and 22.0 at.%, respectively [16]. These transitions are marked by vertical lines in the figures.

According to the dependences, increase in the average positron lifetime in samples with a hydrogen content less than 1.31 at.% is caused mainly by the increasing value of lifetime of the short-lived component τ_f . The increase of the parameter S/S_0 is also evident. At the same time, no long-lived component τ_d was found in the PL spectra. These changes in annihilation characteristics were caused by the crystal lattice expansion induced by hydrogenation, which in turn led to a slight decrease of electron density [8]. This fact was also confirmed by X-ray data analysis.

PL spectra of samples containing (1.31–2.28) at.% of hydrogen revealed the appearance of a long-lived component with the lifetime τ_d varying from 190 ps to 310 ps. However, this component intensity I_d decreased with increasing hydrogen concentration. Values for the short-lived component τ_f and parameters S/S_0 and W/W_0 were practically unchanged. Thus, we can conclude that there was a certain number of vacancies formed in the beginning of this concentration range. With a further increase in hydrogen concentration, the formation of new defects could not be detected, while the existing defects

coagulated together form vacancy clusters and “vacancy-hydrogen” complexes [17].

For samples with hydrogen concentrations varying from 2.28 at.% to 4.23 at.% we detected a slight increase in the lifetime of the short-lived component τ_f and significant decrease of the long-lived component lifetime τ_d . This was accompanied by an increase of its intensity I_d . The increase of hydrogen content from 2.28 at.% to 2.32 at.% was accompanied by a sharp decrease of parameters S/S_0 and W/W_0 . However, the further increase of hydrogen concentration up to 5.10 at.% led only to a gradual decrease of W/W_0 and increase of S/S_0 . The alteration of annihilation characteristics indicates the interaction of hydrogen with vacancy clusters accompanied by the formation of “cluster-hydrogen” complexes. In addition, increased intensity of the long-lived component I_d and altered values of S/S_0 and W/W_0 signal the simultaneous formation of a large number of new defects, mainly of vacancy type [14]. Moreover, the value of lifetime τ_d lies in the range from 225 ps to 190 ps, which corresponds to the annihilation of positrons localized in single vacancies and complexes such as “single vacancy-hydrogen” [18,4]. The increase in lifetime of the short-lived component τ_f indicates that these processes could be accompanied by the formation of dislocations [19], as well as hydride phase formation.

Further increase of hydrogen content in samples from 4.23 at.% to 7.73 at.% was accompanied by the growth of τ_f , τ_d values and parameter W/W_0 , and the drop of the long-lived component intensity I_d and parameter S/S_0 . At the same time, after the hydrogen content reached the value of 5.10 at.%, there was an increase in S/S_0 and a decrease in W/W_0 . Such changes of the annihilation parameters indicate the formation of complexes such as “cluster-hydrogen”. Increasing the hydrogen concentration up to 16.56 at.% reduced the long-lived component lifetime τ_d to 190 ps, and caused growth of its intensity I_d until a value of 21%. At the same time, for the concentrations varying in the range of (7.73–12.14) at.%, the S/S_0 parameter decreased and the W/W_0 parameter increased, whereas in a range of (12.14–16.56) at.% there was only a slight decrease of W/W_0 and an increase in S/S_0 . Thus, this suggests that for the concentration range of (7.73–12.14) at.%, the formation of “cluster-hydrogen” occurs, while in the range of (12.14–16.56) at.% “monovacancy-hydrogen” complexes are formed.

In samples with the hydrogen content of (16.56–31.41) at.%, a sharp increase in the lifetime components τ_f , τ_d , as well as S/S_0 were observed. These processes were accompanied by the reduction of the long-lived component intensity I_d and W/W_0 . This

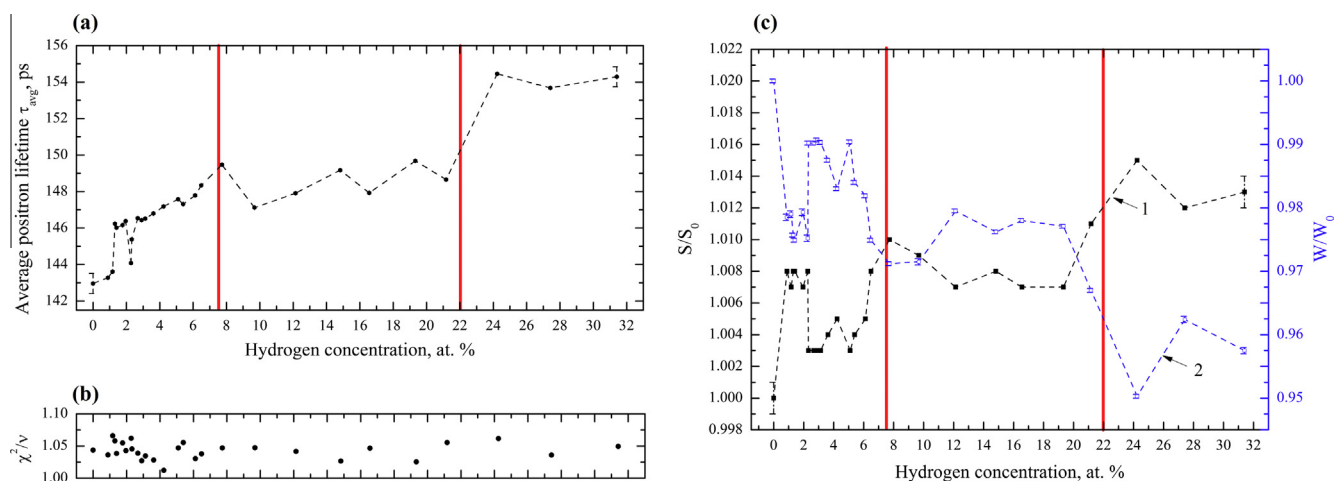


Fig. 1. Dependences of positron annihilation parameters on hydrogen content in commercially pure titanium after gas-phase hydrogenation: (a) average lifetime of positrons; (b) correlation index; (c) relative values of line-shape parameters of DB spectra (1 – S/S_0 and 2 – W/W_0 parameters).

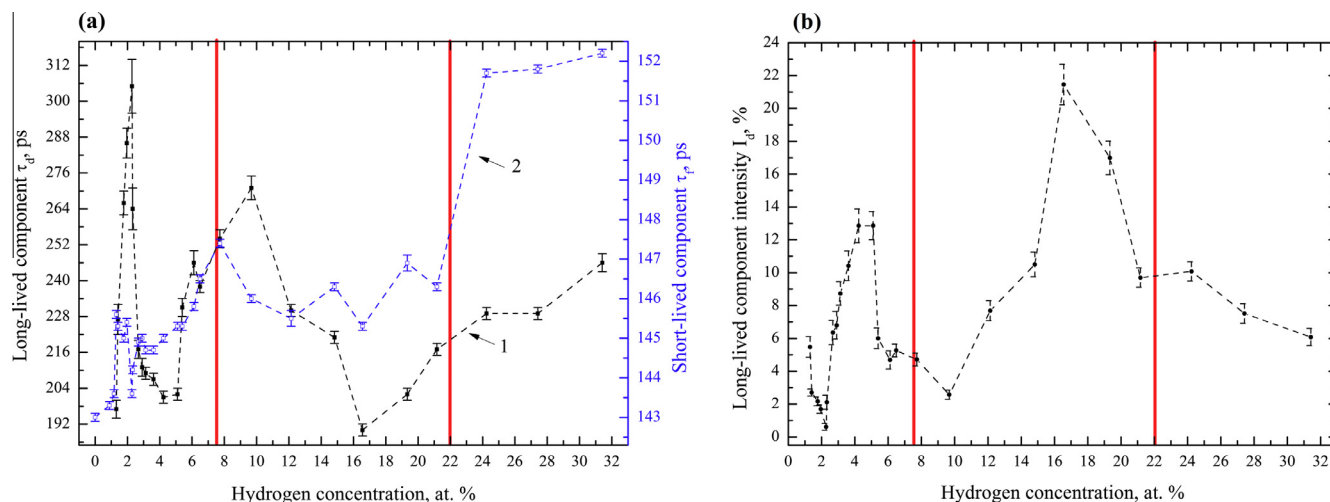


Fig. 2. Dependences of positron annihilation parameters on hydrogen content in commercially pure titanium after gas-phase hydrogenation: (a) positron lifetime values (1 – short-lived component τ_f ; 2 – long-lived component τ_d); (b) intensity of long-lived component I_d .

suggests that, the formation of “defect-hydrogen” complexes, such as “cluster-hydrogen” and “monovacancy-hydrogen” persisted. In this range, the short-lived component lifetime τ_f was equal to 152.0 ± 0.3 ps, which corresponds to the lifetime of positrons in titanium hydride TiH_2 [20]. Hydride formation was also confirmed by X-ray data. According to the X-ray data, the volume fraction of the hydride phase in the titanium samples with the hydrogen content of (24.24–31.41) at.% was equal to 40–50%.

4. Conclusions

This study revealed the behavior of positron annihilation parameters, such as τ_f , τ_d and their corresponding intensities I_f and I_d , as well as the relative changes of parameters S/S_0 and W/W_0 depending on the hydrogen content in commercially pure titanium after gas-phase hydrogenation at 873 K. These results suggest the following:

- For low hydrogen contents (up to 1.31 at.%), the alteration of annihilation parameters was caused by the hydrogenation-induced crystal lattice expansion.
- In the concentration range of (1.31–2.28) at.%, the occurrence of vacancies and vacancy clusters formed mainly due to coagulation of existing vacancies.
- For hydrogen contents from 2.28 at.% to 4.23 at.%, hydrogen interacted with vacancy clusters and complexes such as “cluster-hydrogen” were formed. Moreover, this process was accompanied by the intense formation of single vacancies that subsequently bind with hydrogen atoms and form complexes of the “vacancy-hydrogen” type.
- In the concentration range of (5.10–12.14) at.%, positrons were captured by vacancy clusters containing hydrogen atoms.
- In the concentration range of (12.10–31.41) at.%, positrons were mainly trapped by defects containing hydrogen atoms.
- Since the hydrogenation was carried out in hydrogen at 873 K and was followed by vacuum cooling to room temperature, the processes of defect formation was highly affected, not only by the hydrogen accumulation, but also by the phase transformation processes.

Acknowledgement

The reported study was supported by Russian Government Program “Nauka” (Science), research project No. 1524.

References

- [1] I.P. Chernov, Yu.P. Cherdancev, Yu.I. Tyurin, *Methods of Metal-Hydrogen Systems Study*, Energoatomizdat, Moscow, 2004 (in Russian).
- [2] C.A. Wert, *Topics in Applied Physics*, vol. 29, Springer, Berlin, 1978, pp. 305–330.
- [3] P.V. Geld, R.A. Ryabov, E.S. Kodes, *Hydrogen and Imperfections of the Metal Structure*, Metallurgia, Moscow, 1979.
- [4] J. Čížek, I. Procházka, F. Bečvář, R. Kužel, M. Cieslar, G. Brauer, W. Anwand, R. Kirchheim, A. Pundt, *Phys. Rev. B* 69 (2004) 224106.
- [5] S. Socher, E.V. Lavrov, J. Weber, *Phys. Rev. B* 86 (2012) 125205.
- [6] K. Sakaki, T. Yamada, M. Mizuno, H. Araki, Y. Shirai, *Mater. Trans.* 43 (11) (2002) 2652–2655.
- [7] J. Čížek, I. Procházka, R. Kužel, F. Bečvář, M. Cieslar, G. Brauer, W. Anwand, R. Kirchheim, A. Pundt, *Mater. Sci. Forum* 60 (2004) 445–446.
- [8] K.P. Arefyev, O.V. Boev, O.N. Imas, A.M. Lider, A.S. Surkov, I.P. Chernov, *Phys. Solid State* 45 (1) (2003) 1–5.
- [9] Y.S. Bordulev, R.S. Laptev, V.N. Kudiiarov, A.M. Lider, *Adv. Mater. Res.* 880 (2014) 93.
- [10] R.S. Laptev, Y.S. Bordulev, V.N. Kudiiarov, A.M. Lider, G.V. Garanin, *Adv. Mater. Res.* 880 (2014) 134.
- [11] V.N. Kudiiarov, L.V. Gulidova, N.S. Pushilina, A.M. Lider, *Adv. Mater. Res.* 740 (2013) 690–693.
- [12] D. Giebel, J. Kansy, *Mater. Sci. Forum* 666 (2010) 138–141.
- [13] The SP-program. Electronic source, <http://www.ifj.edu.pl/~mdryzek/page_r18.html>.
- [14] R. Krause-Rehberg, H.S. Leipner, *Positron Annihilation in Semiconductors: Defect Studies*, third ed., Berlin Heidelberg, New York, 2003.
- [15] J.M.C. Robles, E. Ogando, F. Plazaola, *J. Phys.-Condens. Mater.* 19 (2007) 176222.
- [16] A. San-Martin, F.D. Manchester, *Bull. Alloy Phase Diagrams* 8 (1) (1987) 30–42.
- [17] H. Rajainmäki, S. Linderöth, H.E. Hansen, R.M. Nieminen, *J. Phys. F: Met. Phys.* 18 (1988) 1109.
- [18] J. Čížek, I. Procházka, S. Daniš, G. Brauer, W. Anwand, R. Gemma, E. Nikitin, R. Kirchheim, A. Pundt, R.K. Islamgaliev, *Phys. Rev. B* 79 (2009) 054108.
- [19] K. Sakaki, H. Araki, Y. Shirai, *Mater. Trans.* 43 (7) (2002) 1494–1497.
- [20] S.E. Kulkova, O.N. Muryzhnikova, K.A. Beketov, *Int. J. Hydrogen Energy* 21 (11/12) (1996) 1041–1047.