Progress in Natural Science: Materials International 27 (2017) 105–111

Contents lists available at ScienceDirect

Progress in Natural Science: Materials International

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

Original Research

Gas-phase hydrogenation influence on defect behavior in titanium-based hydrogen-storage material

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ARTICLE INFO

Keywords:
Titanium
Hydrogen
Lattice defects
Positron annihilation
Positron lifetime
Doppler broadening

ABSTRACT

Titanium and its alloys are promising materials for hydrogen storage. However, hydrogen penetration accompanies the exploitation of hydrogen storage alloys. In particular, hydrogen penetration and accumulation in titanium alloys changes their mechanical properties. Therefore, the research works of such materials are mainly focused on improving the reversibility of hydrogen absorption-liberation processes, increasing the thermodynamic characteristics of the alloys, and augmenting their hydrogen storage capacity. In the process of hydrogenation-dehydrogenation, the formed defects both significantly reduce hydrogen storage capacity and can also be used to create effective traps for hydrogen. Therefore, the investigation of hydrogen interaction with structural defects in titanium and its alloys is very important. The present work, the hydrogen-induced formation of defects in the alloys of commercially pure titanium under temperature gas-phase hydrogenation (873 K) has studied by positron lifetime spectroscopy and Doppler broadening spectroscopy. Based on the evolution of positron annihilation parameters τ_f, τ_d, their corresponding intensities I_f, I_d and relative changes of parameters S/S_0 and W/W_0, the peculiarities of hydrogen interaction with titanium lattice defects were investigated in a wide range of hydrogen concentrations from 0.8at% to 32.0at%.

1. Introduction

The research of hydrogen interaction with metals is significant for understanding fundamental aspects of hydrogen influence on the properties of structural materials and for solving applied problems, including those related to hydrogen embrittlement of titanium alloys [1–4]. Titanium is frequently used as a component of hydrogen storage materials, and the problem of minimizing their degradation determines the critical importance of such investigations.

Although a considerable amount of works has been carried out on the effect of hydrogen on various properties of titanium alloys, only few studies have been carried out on the hydrogen interaction with structural defects. It has been found that such defects severely affect metal characteristics and can reduce the capacity of hydrogen storage materials. Further more hydrogen has high diffusion mobility and reactivity in metals, which leads to the formation of complex defects, including vacancy-type defects, impurity atoms, dislocations, interstitial atoms and grain boundaries.

Positron annihilation (PA) techniques such as positron lifetime spectroscopy (PLS) and Doppler broadening spectroscopy (DBS) are promising nuclear physics methods for investigating structural defects in metal-hydrogen systems. The efficiency of PA methods for studying metal-hydrogen systems was demonstrated in the previous studies [5–11]. For instance, these methods may study the mechanisms and dynamics of defects generatin, transformation and disappearance of the defects during hydrogenation. In particular, PLS can determine the type of defects, track the dynamics of their concentration and size during hydrogenation. DBS can be used to investigate the structure changes, phase transitions and chemical composition. Furthermore, simultaneous use of PLS and DBS techniques, together with conventional methods of X-ray diffraction (XRD) and scanning electron microscopy (SEM), enables more detailed behavior of hydrogen interaction with titanium.

Hydrogen interaction with titanium strongly depends on temperature. According to the Ti-H phase diagram (Fig. 1) hydrogen solubility in titanium at room temperature is small, and hydrogenation leads to δ-hydride formation. Hydrogen solubility in titanium increases with temperature, and hydride immediately forms after exceeding the level of hydrogen solubility in the region of phase diagram below the line of 573 K. There are phase transitions followed the sequence of α+β-phase,

Peer review under responsibility of Chinese Materials Research Society.
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http://dx.doi.org/10.1016/j.pnsc.2017.01.001
Received 9 October 2016; Accepted 30 November 2016
Available online 30 January 2017

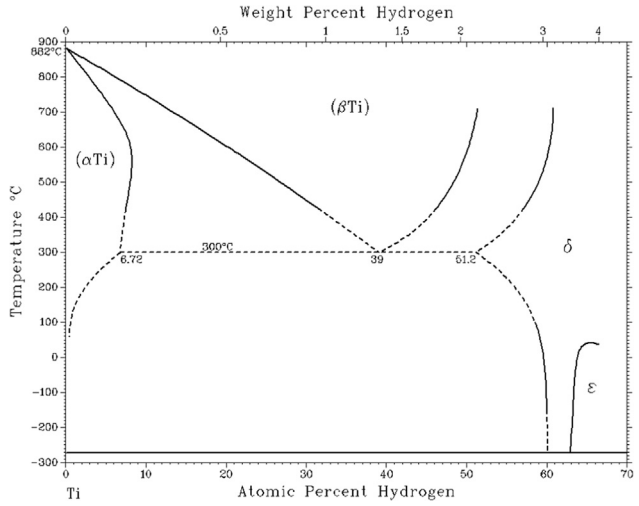

Fig. 1. Ti-H phase diagram [12].

β-phase, β+δ-phase and δ-phase during hydrogenation at temperatures higher than 573 K.

After cooling down to room temperature from any of the afore mentioned phase areas, the titanium-hydrogen system transits into α+δ-phase. Thus, the effect of hydrogen on structural defects in titanium strongly depends on hydrogenation temperature and hydrogen concentration. Interestingly, the systematic investigation in this field has not yet been performed. Hence, in the present study the hydrogen interaction with structural defects in titanium under gas-phase high-temperature hydrogenation (873 K) and subsequent slow cooling (1.5 K/min) were investigated by means of electron-positron annihilation.

2. Material and experimental

Commercially pure titanium alloy was used for this investigation since this single-phase material is a good test material for studying hydrogenation-induced defect formation. The surface of flat rectangular (30×30×1 mm) samples was mechanically polished, and then the samples were annealed in vacuum at 923 K for 1 h.

The samples were hydrogenated on automated complex Gas Reaction Controller LPB (Advanced Material Corporation) up to the specified concentration at the hydrogen pressure of 67 kPa and temperature of 873 K (with the heating rate of 4 K/min). Subsequent cooling was performed in vacuum at the rate of 1.5 K/min. The hydrogen concentration was measured by manometric method during hydrogenation and then with the help of RHEN602 hydrogen analyzer (LECO).

The phase composition and structural parameters of the samples before and after the hydrogenation were studied using the XRD-6000 diffractometer with a CuKα radiation source. Phase composition analysis was performed using the PCPDFWIN database and POWDER CELL 2.5 full profile analysis software. The surface of the samples after hydrogenation was investigated with Philips SEM 515 scanning electron microscope.

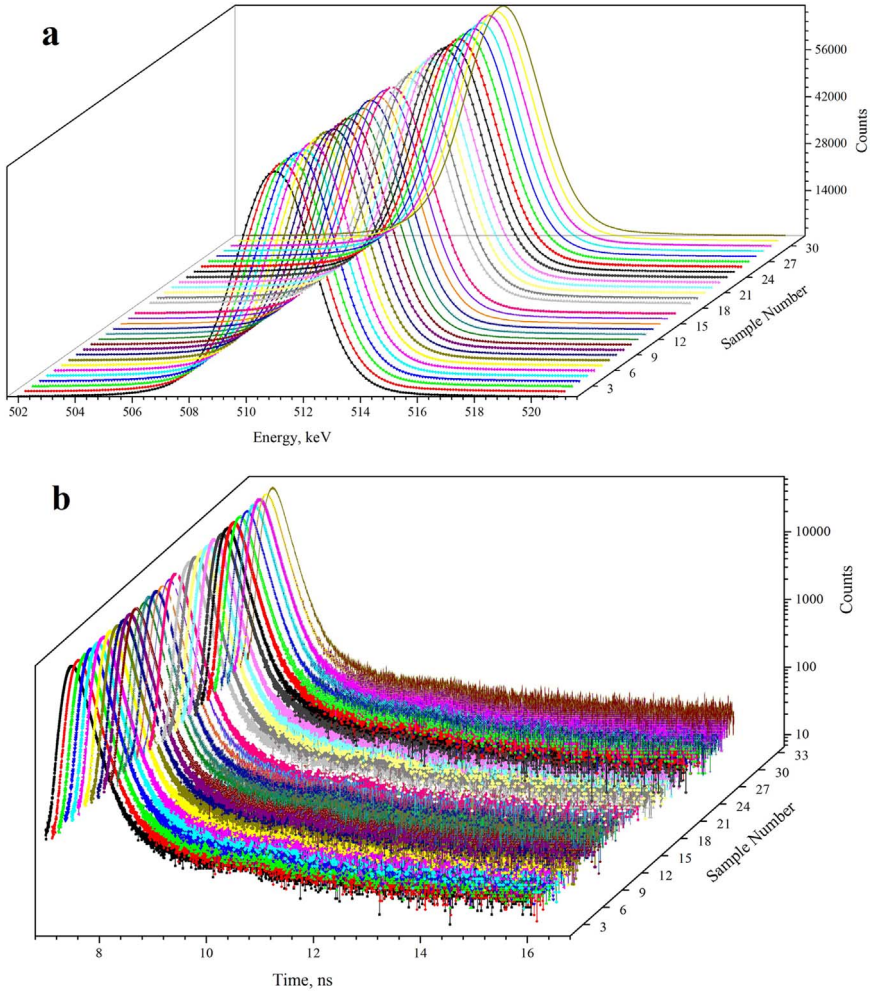

Fig. 2. Spectra of (a) positron lifetime and (b) Doppler broadening shift of annihilation photons in the annealed titanium samples before hydrogenation.