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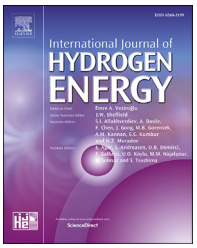

Characterization of defects in titanium created by hydrogen charging

Petr Hruška [a,*], *Jakub Čížek* [a], *Jan Knapp* [a], *František Lukáč* [a], *Oksana Melikhova* [a], *Silvie Mašková* [a], *Ladislav Havela* [a], *Jan Drahokoupil* [b]

[a] *Faculty of Mathematics and Physics, Charles University, Ke Karlovu 3, 121 16 Prague, Czech Republic*
[b] *Institute of Physics of the Czech Academy of Sciences, Na Slovance 2, 182 21 Prague, Czech Republic*

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ABSTRACT

In the present work positron annihilation spectroscopy was employed for investigation of defects created in titanium by hydrogen loading. Pure titanium samples were firstly annealed to remove dislocations introduced by cutting and polishing. Subsequently the samples were loaded with hydrogen up to various hydrogen concentrations. Ti samples with different microstructures were compared: (i) conventional coarse grained sample, (ii) ultra fine grained material with microstructure refined by severe plastic deformation. Hydrogen gas loading of coarse grained and ultra fine grained samples was performed at hydrogen gas pressure of 103 bar and temperature of 150 °C. This resulted in formation of δ-TiH_x phase in Ti matrix. The hydrogen content absorbed in the samples was determined by thermogravimetric analysis. The phase composition of hydrogen-loaded samples was characterized by X-ray diffraction. Hydrogen loading introduced vacancies which agglomerated in the sample into small vacancy clusters. In addition to vacancies, dislocations were created by α-Ti → δ-TiH_x phase transition. Differential thermal analysis revealed that hydrogen is trapped at several kinds of traps characterized by different binding energies. The release of hydrogen from these traps precedes the decomposition of the δ-TiH_x phase.

Introduction

Titanium and titanium based alloys are attractive modern structural materials with excellent specific strength and stiffness, relatively low density and high corrosion resistance [1]. Mechanical properties of Ti and Ti-based alloys can be remarkably improved by grain refinement [2]. Severe plastic deformation (SPD) [3] is a method enabling to achieve an extreme grain refinement down to nanoscale. By repeated application of SPD ultra fine grained (UFG) bulk materials with grain size in the range of 100–500 nm can be produced. SPD processing also enhances corrosion resistance and biocompatibility [4]. Commercial purity UFG Ti prepared by SPD was already successfully used for dental implants [5]. UFG materials are characterized by strongly non-equilibrium structure with high density of dislocations and grain boundaries often leading to unique physical properties, in particular

* Corresponding author.
E-mail address: peta.hruska.l@gmail.com (P. Hruška).
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abnormally high diffusion activity and strength enhancement [3]. High-pressure torsion (HPT) [6] is the most efficient SPD technique for grain refinement developed so far. In HPT processing a disc-shaped sample placed between two anvils is compressed by a pressure of several GPa and simultaneously subjected to torsion strain by rotating of one of the anvils.

In many technological applications hydrogen comes into contact with Ti or Ti alloys. Hydrogen absorption in Ti lattice leads to a degradation of its mechanical properties, so-called hydrogen-assisted cracking (HAC) [7–9]. It is known that the formation energy of open-volume defects is lowered in the presence of hydrogen absorbed in the lattice due to positive binding energy between hydrogen and defects leading to hydrogen segregation at defects [10–12]. Lattice defects also affect the kinetics of hydrogen absorption in Ti lattice. Hence the role of defects and their interaction with hydrogen must be understood in order to elucidate the mechanism of HAC.

At normal pressure Ti naturally occurs in hcp α-Ti phase below the temperature of 882 °C when it is transformed to high temperature fcc β-Ti [13]. At high pressures hcp ω-Ti phase is formed. According to the phase diagram of TiH system [13] hydrogen loading at temperatures above 298 °C or at high H_2 pressures leads to formation of fcc δ-TiH_x phase with fcc structure. In the δ-TiH_x phase hydrogen ions occupy tetrahedral sites in fcc cubic lattice [14,15] and hydrogen content in this phase varies in the range $x_H \approx 1.6–2.0$ H/Ti [13].

In the present work hydrogen absorption in coarse grained (CG) and UFG Ti prepared by HPT was compared. Positron annihilation spectroscopy (PAS) [16] was employed for investigation of hydrogen interaction with defects. PAS is a well developed non-destructive technique with a high sensitivity to open-volume defects, like vacancies, dislocations, vacancy clusters etc. Defect studies by means of PAS were accompanied by structural characterization using X-ray diffraction (XRD) and investigation of thermal stability of absorbed hydrogen by differential thermal analysis (DTA) combined with thermogravimetry (TG).

Experimental details

Bulk Ti samples with purity of 99.7% were studied in the present work. All samples were first annealed at 1000 °C for 2 h in vacuum (10^{-3} mbar) in order to remove all defects introduced by previous cutting and shaping of the samples. Two sets of samples were studied: (a) CG samples of annealed material and (b) UFG samples prepared by HPT deformation. The UFG structure was fabricated by HPT straining at room temperature under a pressure of 6 GPa using 5 revolutions. The UFG samples exhibited grain size around 150 nm.

Both CG and UFG samples were hydrogenated using various methods of hydrogen loading: (i) electrochemical charging at room temperature with a constant current of 20 mA applied for 240 h in an electrolyte consisting of H_3PO_4 and glycerine in the volume ratio 1:2; (ii) high-temperature H_2 gas loading at 500 °C and moderate H_2 pressure of 0.6 bar for 1 h and 50 h; (iii) low-temperature H_2 gas loading at 150 °C and high H_2 pressure of 103 bar for 100 h.

Positron lifetime spectroscopy (LT) was employed for investigation of hydrogen-induced defects. LT measurements were performed on a digital spectrometer [17] with time resolution of 145 ps (FWHM of the resolution function). At least 10^7 positron annihilation events were collected in each LT spectrum, which was subsequently decomposed into exponential components using a maximum likelihood method [18]. The contribution of positrons annihilated in the source has been always subtracted from measured LT spectra.

Phase composition and lattice parameters of samples studied were determined by XRD measurements in the Bragg–Brentano symmetric geometry using Co K_α ($\lambda = 1.79$ Å) radiation.

Thermal stability of Ti samples and desorption of hydrogen were studied by simultaneous DTA and TG measurements carried out in a Setaram Labsys Evo apparatus. The samples were heated and cooled in Al_2O_3 crucibles using the rate of 5 K/min. The DTA/TG measurements were performed in a protective Ar atmosphere (20 sccm). Gases desorbed from the samples were analyzed by a quadrupole mass spectrometer attached to the DTA/TG apparatus.

Results and discussion

Virgin samples

Fig. 1a shows XRD pattern for the CG sample. Only reflections for α-Ti phase are present in the pattern. The lattice parameters $a = 2.95057(4)$ Å and $c = 4.6863(4)$ Å obtained from the Rietveld refinement of the XRD pattern agree well with the values reported for α-Ti in literature [19]. The CG Ti sample exhibits single component positron lifetime (LT) spectrum with lifetime of 144.6(6) ps, see Table 1. This value is close to the bulk Ti lifetime $\tau_B = 147$ ps [21] obtained by ab-initio theoretical calculations. This testifies that the concentration

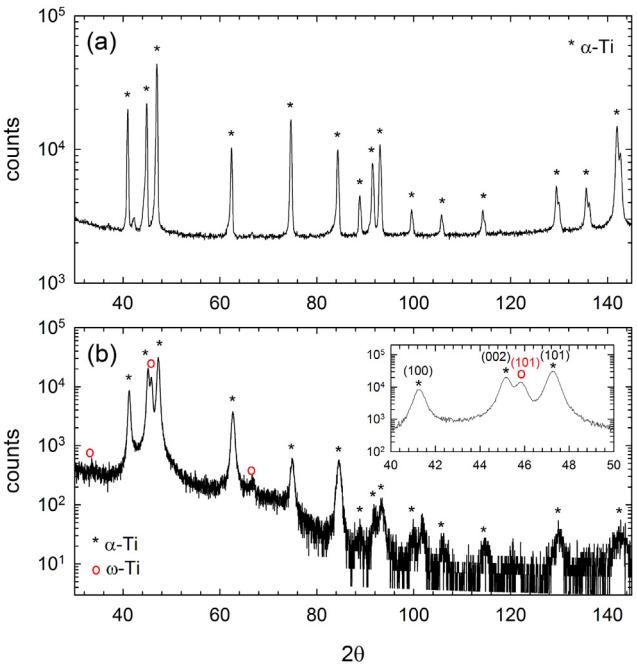

Fig. 1 – XRD patterns for (a) virgin CG Ti, (b) virgin UFG Ti. The inset shows a detail of the XRD pattern for the UFG sample with (101) reflection of the ω-Ti phase.

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