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Reversible hydrogen absorption in a Ti-6Al-4V alloy produced by mechanical alloying

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ARTICLE INFO

Article history:

Received 5 June 2014

Received in revised form

21 July 2014

Accepted 27 July 2014

Available online 19 August 2014

Keywords:

Hydrogen absorbing materials

Titanium alloys

Mechanical alloying

Crystal structure

Neutron diffraction

ABSTRACT

Hydrogen absorption in a Ti-6Al-4V alloy prepared by ball milling was investigated in view of the reversible storage of hydrogen in a solid state. The material characterization by X-ray and neutron diffractometry demonstrated the formation of a single α phase whose unit cell expanded during the hydrogen absorption. The maximum storage capacity of this α phase was 1.8 wt% H and no hydride formation was observed. The existence of such a particular supersaturated hexagonal phase was attributed to the strongly defective structure formed by the mechanical alloying process.

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Introduction

The Ti-6Al-4V alloy is mainly known for its applications in the nuclear, marine and aerospace field [1], however more recently this alloy has been studied as a possible system to store hydrogen in a solid state for its ability to accumulate significant amounts of hydrogen in a reversible manner [2]. In fact, one of the major causes limiting the use of hydrogen as “energy carrier” for automotive applications is its low energy density per unit volume and the difficulty to store enough hydrogen for a sufficient autonomy inside a vehicle [3].

The hydrogen storage in solid matrices is considered a possible alternative to technologies based on high pressure

storage (~70 MPa), or cryogenic storage (at 21 K) in a liquid state. From this point of view, Ti and Ti-based alloys are considered interesting material due to their affinity with hydrogen, which is able to diffuse into the material structure forming stable compounds [4]. Hydrogen diffusion in titanium alloys has been primarily studied because of the degradation of the mechanical properties caused by the formation of brittle hydrides microstructures even at near-room temperatures [4,5]. Hydrogen, however, has also been investigated as a temporary alloying element in titanium alloys to modify the material microstructure [5–7].

Ti-6Al-4V is a α/β titanium alloy whose microstructure is determined by the two phases, α and β , that are obtained in due quantities by thermo-mechanical processes for

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<http://dx.doi.org/10.1016/j.ijhydene.2014.07.149>

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optimum mechanical properties [8]. The α phase is thermodynamically stable at low temperature and has a hexagonal close-packed (hcp) structure while the body-centered cubic (bcc) β phase shows a transus temperature of about 900 °C [5,8]. However, the relative stability of the two phases is influenced by the alloying elements. Al, in fact, strongly stabilizes the α phase extending its existence towards higher temperatures [9]. On the contrary, V is a β stabilizer component that contributes to retain the bcc crystal structure at room temperature [10,11].

Even if hydrogen diffuses easily in titanium alloys, its solubility in the two phases is different. The hexagonal packing of the α phase can hold hydrogen in solid solution only at low concentration (<0.3 wt% H) [12] because of the distortion caused by the interstitial hydrogen atoms to the hexagonal cell. For hydrogen content higher than 0.3 wt% a new phase, the δ hydride (fcc structure), begins to precipitate from the supersaturated instable α phase, up to ~ 3 wt% H (H/Ti = 1.5) when all the remaining titanium transforms to the δ phase [4,13]. In the β phase hydrogen diffuses preferentially and its solubility is higher because of the bcc structure [13]. Hydrogen, in fact, is considered a stabilizer of the β phase [12] because it decreases the α – β phase transformation temperature and, consequently, a destabilizer of the low temperature α phase [4,14]. However, increasing the hydrogen content, the precipitation of the δ hydride has been observed in the β phase too [4].

In this work, we investigated the microstructural effects of hydrogen absorption in a Ti-6Al-4V alloy obtained by ball milling for possible storage applications [2,4,5,12,18]. Ball milling is a method of alloying metallurgical powders whose characteristics can be particularly attractive for the specific application considered in this study. The alloys obtained by ball milling, in fact, compared to traditional methods show a typical nanoscale morphology in which non-equilibrium, amorphous and, sometimes, new transition phases have been observed [15–17].

The material prepared has shown a storage capacity of 1.8 wt% H, still low for an on-board storage system, but the novelty was that hydrogen absorbed in a supersaturated metastable α phase with no evidence of hydrides precipitation. Such a result could be relevant in view of a reduction of the reaction enthalpy of the reversible hydrogenation process, which is known being an important limit in the use of metal hydrides as solid storage systems [19,20].

Material and methods

Sample preparation

Ti powder (99.5 wt%, $d < 75 \mu\text{m}$, Alfa Aesar), Al and V powders (99.5 wt%, $d < 45 \mu\text{m}$, Alfa Aesar) have been mixed according to the final alloy composition Ti-6Al-4V (Ti = 90 wt%, Al = 6 wt%, V = 4 wt%) and mechanically alloyed by ball milling in a high-energy mixer mill (Retsch MM 301) for 15 h at a vibration frequency of 15 Hz. The process was conducted at room temperature with a ball-to-powders (mass) ratio of 10:1 [17]. The mill uses two tungsten carbide grinding jars and each jar was charged with 2.5 g of powder mixture (dry milling) for a total of

5 g of product for run. The pressure in the grinding jars was atmospheric.

Hydrogen absorption

After alloying, the powder was hydrogenated using the system shown in Fig. 1. All samples before absorption were pre-treated according to the following procedure: the powder was charged in a stainless steel (AISI 316L) vessel, heated under vacuum ($P = 5 \cdot 10^{-2}$ Pa) to $T = 600$ °C for 60 min and let to cool to room temperature under vacuum. Such a preliminary treatment was carried out to limit the dissolution of nitrogen and oxygen into the material bulk. The system was then filled with H_2 increasing pressure up to $P = 100$ kPa and temperature to $T = 500$ °C and kept in these conditions for 120 min. Afterwards, the system was evacuated ($P = 5 \cdot 10^{-2}$ Pa, $T = 600$ °C, 60 min) and finally filled again with hydrogen ($P = 100$ kPa, $T = 500$ °C) for 60 min. The process steps are resumed in Table 1. The hydrogenation temperature was determined on the base of preliminary tests (not reported for the sake of brevity) performed to find the best combination between hydrogenation time and hydrogen absorbed quantity. Being the hydrogenation carried out at relatively low pressure, the high temperature was needed to improve the hydrogen diffusion into the material.

The amount of hydrogen desorbed by the alloy was evaluated by Temperature Programmed Desorption (TPD, Micro-metrics ChemiSorb 2750). This method has the advantage of correlating the desorbed quantity with temperature, an important parameter in reversible hydrogen storage. In a typical measure a powder sample of 25 mg was loaded in a quartz tube and heated by flowing argon up to $T = 1000$ °C, with a heating rate of 10 °C/min. The desorption pressure was atmospheric. The TPD apparatus is equipped with a cold trap (–100 °C) for condensable gases and water vapour, located up line of the analyzer. The TPD signal was calibrated by using titanium hydride as standard (99.0 wt% TiH_2 , Alfa Aesar).

Scanning electron microscopy

The morphological characterization of metal powders before and after treatments was conducted by Scanning Electron Microscopy SEM (JEOL 5600LV). Some powder particles after mechanical alloying were embedded in epoxy resin and sliced

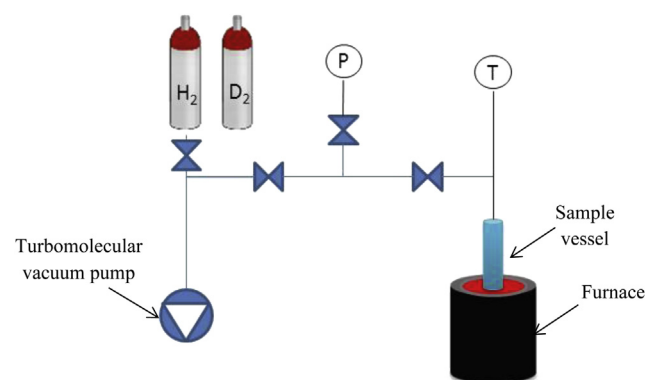


Fig. 1 – Diagram of the hydrogen absorption apparatus.

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