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Hydrogen cracking in titanium-based alloys

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Abstract

In this paper the phenomena of hydrogen cracking and hydrogen-induced second phases formation in titanium based alloys is discussed in detail, addressing to three different alloys; the alpha + beta Ti–6Al–4V alloy, the metastable Beta-21S and the Ti–20 wt.%Nb refractory alloy. The prior microstructure of the alloy plays a very significant role on its behavior under exposure to a hydrogen-containing environment. In the Ti–6Al–4V alloy the main mechanism of hydrogen cracking is the formation and rupture of brittle titanium hydride phases. The severity of hydrogen degradation in the Ti–6Al–4V alloy depends on the amount and distribution of the β phase in the microstructure due to a more rapid diffusion transport of hydrogen in the bcc β phase. On the other hand, the Timetal Beta-21S β alloy, exposed to the electrochemical (high fugacity) hydrogen environment at room temperature, exhibits a fair resistance to hydrogen. In the Ti–20 wt.%Nb alloy hydrogen-induced phase transitions and hydrides formation were followed by an interesting softening effect, irrespective of the charging procedure.

Keywords: Titanium alloys; Cracking; Hydrides; Ti–6Al–4V; Beta-21S; Ti–Nb alloys

1. Introduction

Titanium based alloys are attractive for many structural applications requiring light weight and good elevated temperature behavior. Although titanium is generally considered to be reasonably resistant to chemical attack, severe problems can arise when titanium based alloys come in contact with a hydrogen containing environment [1]. The severity and the extent of the hydrogen interaction with titanium based alloys are directly related to the microstructure and composition of the titanium alloys. As a consequence of the different behavior of hydrogen in alpha and beta phases of titanium, the susceptibility of each of these phases to the various forms and conditions of hydrogen embrittlement can vary significantly [2]. In this paper the phenomena of hydrogen cracking and hydrogen-induced second phases formation in titanium alloys is discussed in detail regarding three different alloys. The first part will address to some hydrogen effects in Ti–6Al–4V alloy, which, up to date, is the most widely used among titanium alloys. In the second part, the influence of hydrogen on Timetal Beta-21S, a metastable beta titanium alloy developed for improved properties and especially oxidation resistance, is presented. Finally, the third part of the paper will describe some hydrogen effects on the Ti–Nb refractory system, where the Ti–20 wt.%Nb is the selected representative alloy.

2. Experimental

The titanium alloys used for this study were Ti–6Al–4V, Timetal Beta-21S and Ti–20 wt.%Nb alloys. The Ti–6Al–4V alloy was thermo-mechanically treated in two microstructural conditions; duplex microstructure as a result of a duplex-annealing process, and fully lamellar microstructure resulted from a beta-annealing procedure. The exact thermo-mechanical treatment of the above alloy is described in detail elsewhere [3]. The Timetal Beta-21S alloy was received in the mill annealed condition, in the form of 1.2 mm thick rolled sheet. Prior to electrochemically hydrogen charging, the material was aged to peak strength at 538 °C for 8 h in vacuum and both as-received and aged specimens were investigated. The Ti–20 wt.%Nb alloy was prepared by cold-sintering, at 30 kbar, followed by 12 h annealing at 1000 °C. Specimens

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from these alloys were exposed to either electrochemical (high fugacity) or gas-phase (low fugacity) hydrogen charging. The amount of hydrogen absorbed is measured using a LECO RH-404 hydrogen determinator. The microstructure of the as-received as well as hydrogenated specimens was investigated by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM). In addition, microhardness tests were performed, using a Matsuzaura MHT-1 Micro-Hardness Tester, at room temperature.

3. Results and discussion

3.1. Hydrogen effects on Ti–6Al–4V alloy

The titanium based alloy considered in this section is made up of a combination of the hcp alpha phase and bcc beta phase and is thermo-mechanically treated in two distinguished microstructures, duplex and fully lamellar, as described in Fig. 1.

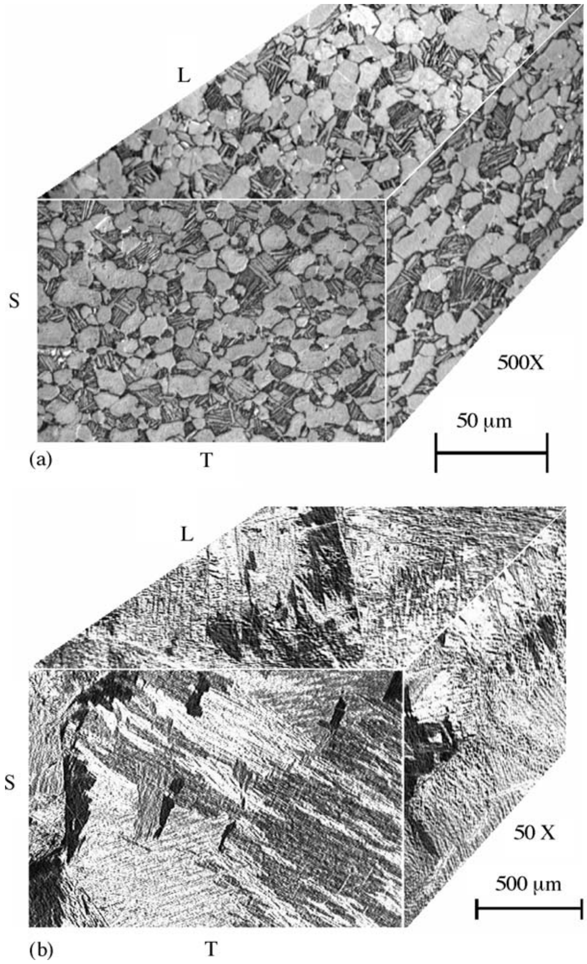

Fig. 1. Ti–6Al–4V alloy after thermo-mechanical treatment: (a) duplex microstructure showing equiaxed primary α and lamellar packets of transformed β/secondary α; (b) fully lamellar microstructure showing continuous β phase.

Hydrogen content measurements (by means of a LECO RH-404 hydrogen determinator system), conducted on the above Ti–6Al–4V specimens after electrochemical hydrogenation in a 1:2 (vol.) H_3PO_4:glycerine solution [2], or after gaseous-phase charging at 5 atm, 350 °C for 5 h [3], revealed that the hydrogen concentrations absorbed in the fully lamellar alloy is always higher than in the duplex microstructure, irrespective of the charging conditions. Since the rate of hydrogen diffusion is higher by several orders of magnitude in the β phase than in the α phase [4], microstructures with more continuous β phase, such as fully lamellar microstructure (Fig. 1a), will absorb more hydrogen than those with discontinuous β, such as the fine equiaxed α in the duplex microstructure (Fig. 1b). In the group IV transition metals hydrogen tends to occupy tetrahedral interstitial sites [5]. The higher solubility, as well as the rapid diffusion (especially at elevated temperatures) of hydrogen in the beta titanium results from the relatively more open body center cubic (bcc) structure in comparison to the hexagonal closed packed (hcp) lattice of alpha titanium.

The presence of hydrogen in solid solution in both α and β phases results in lattice expansions. In the electrochemically hydrogenated specimens, precipitation of the tetragonal γ-TiH occurred initially at relatively low hydrogen concentrations, which was followed by the formation of the tetragonal δ-TiH_x with the increase in the hydrogen concentration. Due to the lower solubility of hydrogen in the α phase [6], the hydrides precipitation in the duplex microstructure occurred at lower hydrogen concentrations in comparison to the alloy with a fully lamellar microstructure and a more continuous β-phase. In the gas-phase charged specimens no hydrides precipitation occurred (due to the relatively small absorbed contents), however, an increase in the dislocations density followed by enhancement of their movement was observed [3].

Hydrogen damage of titanium and its alloys is manifested as a loss of ductility (embrittlement) and/or reduction in the stress-intensity threshold for crack propagation [7]. In alpha + beta titanium alloys the main mechanism of hydrogen embrittlement was often suggested to result from the precipitation and decomposition of brittle hydride phases. At lower temperatures, the titanium hydride becomes brittle and severe degradation of the mechanical and fracture behaviors of these alloys can occur [1]. When a significant amount of β phase is present, hydrogen can be preferentially transported within the β lattice and will react with the α phase along the α / β boundaries. Under these conditions, degradation will generally be more severe with severity of degradation reflecting the hydrogen pressure dependence of hydrogen transport within the β phase [8]. Hydrogen-induced cracking is related also to the environment. During cathodic charging and exposure to electrolytic solution of duplex and fully lamellar Ti–6Al–4V alloy, we observed that hydride formation and cracking will usually take place in the α phase or along α / β interface, depending on the prior microstructure of the alloy (Fig. 2) [2].

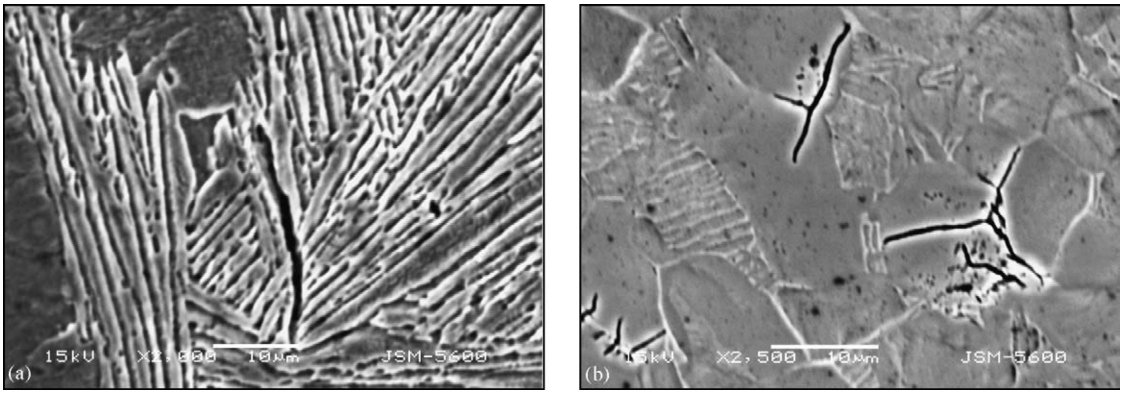

Fig. 2. SEM micrographs of Ti–6Al–4V alloys after electrochemical hydrogenation ($1H_3PO_4$:2 glycerine, 50 mA/cm^2, 69 h) revealing hydrogen-induced cracking in: (a) the fully lamellar microstructure, between the α and β lamellas; (b) duplex microstructure, in the boundaries and inside the equiaxed grains of primary α [2].

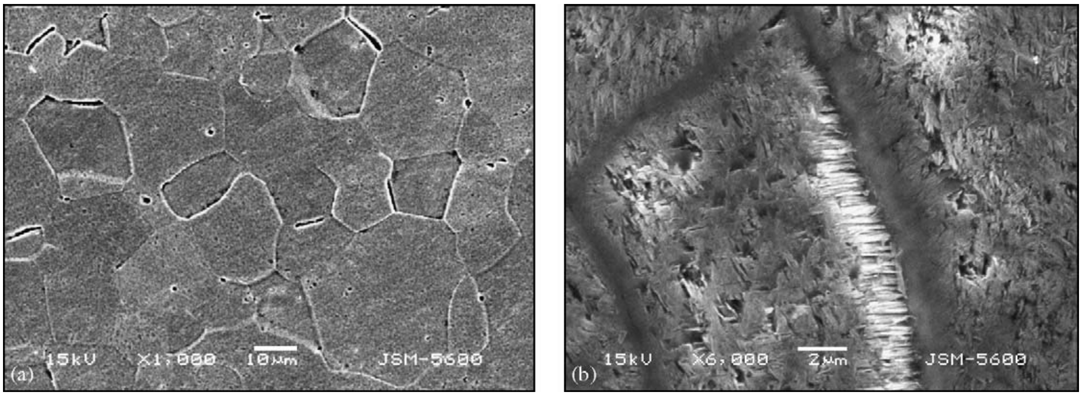

Fig. 3. Microstructure of Timetal Beta-21S alloy: (a) before and (b) after peak-aging at 538 °C for 8 h.

3.2. Hydrogen effects on Beta-21S alloy

The titanium alloy discussed in this section in his as-received mill-annealed condition is made up only of bcc β phase. After peak aging at 538 °C, the acicular hcp α phase precipitated in the β-matrix (Fig. 3) and the alloy consists of both α and β phases, as shown in the X-ray diffraction pattern in Fig. 4.

Both specimens were exposed to electrochemical hydrogenation in a 1:2 H_3PO_4:glycerine (vol.) solution, at 50 mA/cm^2, for different charging times. The kinetics of hydrogen absorption are presented in Fig. 5. Comparing between the absorption plots, at shorter charging times, the amount of hydrogen absorbed in the as-received mill-annealed specimen, consisting only of the bcc β phase, is higher. The slower increase of the absorbed hydrogen concentrations in the aged alloy at shorter charging times can

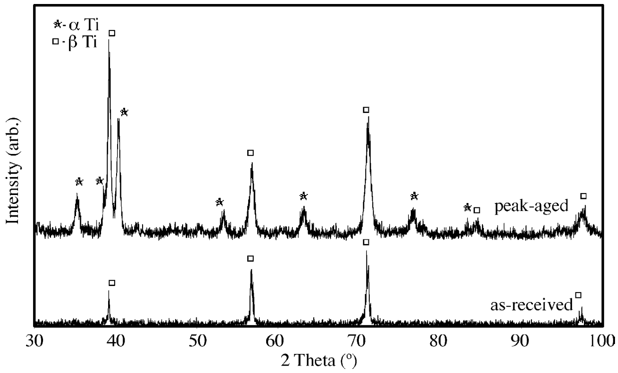

Fig. 4. X-ray diffraction pattern of as-received and peak-aged Timetal Beta-21S alloy.

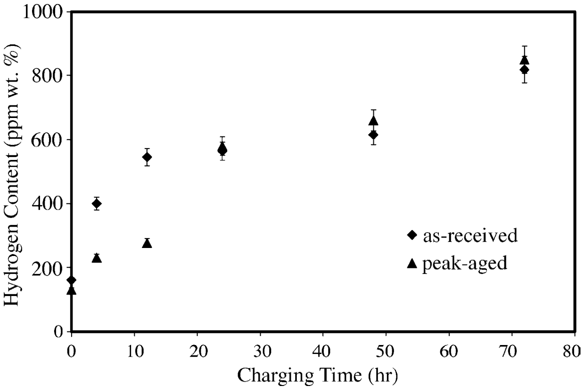

Fig. 5. Hydrogen absorption in as-received and aged Timetal Beta-21S alloy.

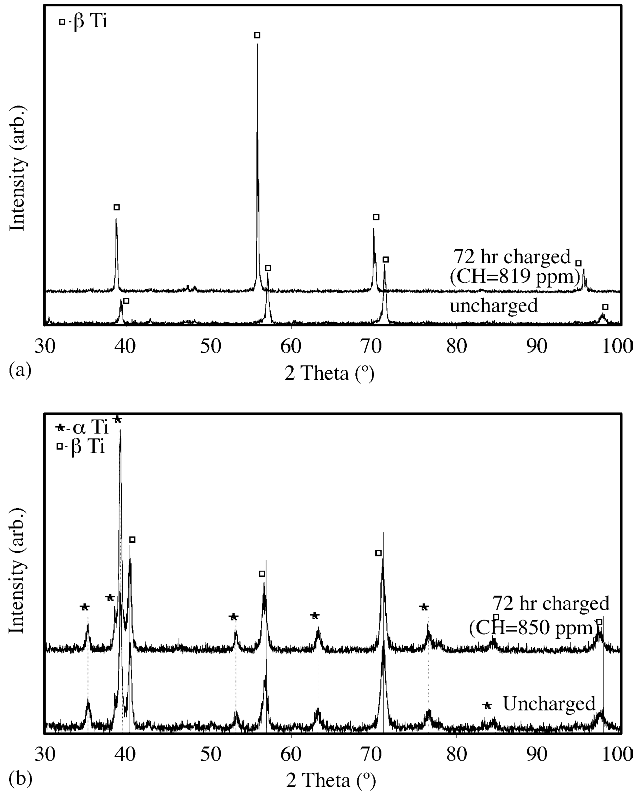

Fig. 6. X-ray diffraction patterns of uncharged and 72 h hydrogenated: (a) as-received and (b) peak-aged Timetal Beta-21S alloy.

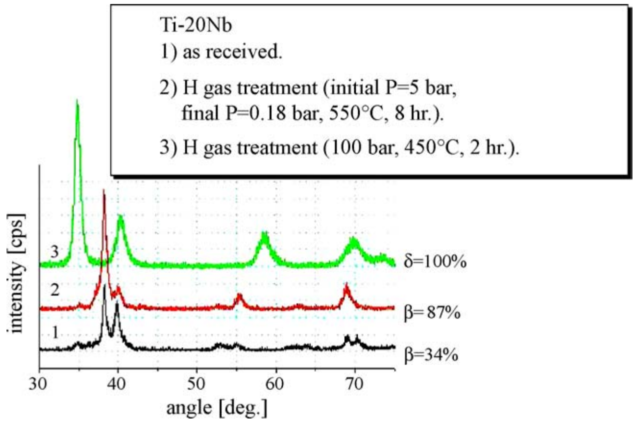

Fig. 8. X-ray diffraction patterns of Ti–20 wt.%Nb alloy before and after gas-phase hydrogenation at different charging conditions.

be explained by the existence of the hcp α phase, in which hydrogen solubility is very small, especially at room temperature. However, after 24 h of charging, the hydrogen uptake increases so drastically in the aged material, that it equals the concentration absorbed in the as-received specimen. From this point, the increase in the absorbed hydrogen concentration is almost the same for both specimens.

On exposure to electrochemical hydrogen environment, hydrogen-induced strain in both as-received and aged specimens. The β peaks shifted to lower angles, i.e., higher *d* spacings and higher *a* values in both X-ray diffraction patterns (Fig. 6). However, in the as-received alloy, the expansion of the β-phase's lattice parameter is higher than in the aged alloy (0.6% maximum increase of the lattice parameter after 72 h of charging in comparison to 0.4%). In the aged alloy the influence of hydrogen on the α-phase's cell parameters was insignificant.

No hydrides precipitation was observed. Scanning electron microscope (SEM) investigations did not reveal hydrogen-induced cracking in both specimens. The alloy exhibits good resistance to hydrogen embrittlement at room temperature in an electrochemical environment.

3.3. Hydrogen effects on Ti–20 wt.%Nb alloy

Until now, some work has been conducted on processing and mechanical behavior of Ti–Nb alloys, but very few results are known about the non-equilibrium conditions of phase transformations in Ti–Nb alloys, as well as the change of mechanical properties due to hydrogen exposure. The exposure of Ti–20 wt.%Nb alloy to high fugacity hydrogen (electrochemical hydrogenation) led to the transformation of $\alpha + \beta$ into $\alpha + \beta + (\mathrm{Ti, Nb})\mathrm{H}_x$. The microhardness of the alloy decreased significantly, probably due to the change

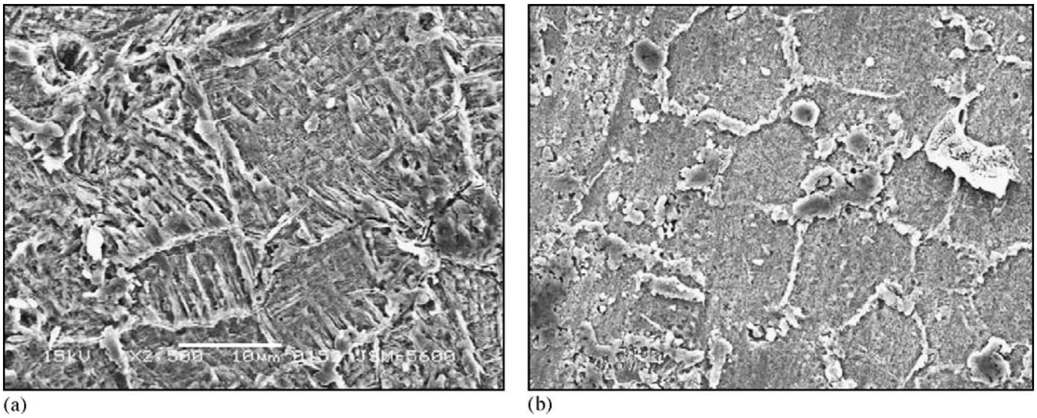

Fig. 7. SEM examination of Ti–20 wt.%Nb alloy: (a) before and (b) after gas-phase hydrogenation.

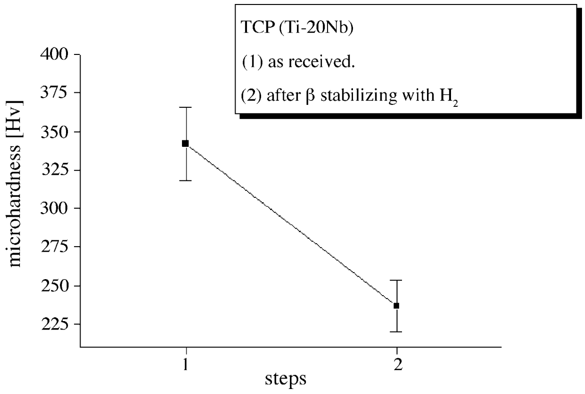

Fig. 9. Microhardness values of Ti–20 wt.%Nb alloy before and after gas-phase hydrogenation.

in the α / β ratio during the precipitation of (Ti,Nb)H_x [9].

Exposure to low fugacity hydrogen (gas-phase hydrogenation) resulted into a change in the microstructure presented in Fig. 7. Exposure to low fugacity hydrogen (gas-phase hydrogenation) at 5 bar, 550 °C for 8 h stabilized and increased the percentage of the β phase from 34% in the untreated alloy to 87%, while during exposure to 100 bar, 450 °C, for 2 h, the X-ray diffraction pattern revealed the sole existence of the δ Ti-hydride phase (Fig. 8).

The hydrogen-induced phase transformation in the Ti–20 wt.%Nb alloy was followed by a significant decrease in the microhardness of the alloy (Fig. 9), the softening effect very similar to that observed in the high fugacity hydrogenated alloy (electrochemical charging).

4. Summary

Titanium based alloys are important structural materials, particularly to the aerospace industry, because of their low density, good mechanic properties and superior corrosion resistance. However, problems arise when hydrogen comes in contact with these alloys, due to the great affinity of titanium for hydrogen. Hydrogen cracking and hydrogen-induced second phases formation were demonstrated on the Ti–6Al–4V alloy, thermo-mechanically treated to a duplex and a fully lamellar microstructures, on the Timetal Beta-21S alloy, and on the refractory Ti–25 wt.%Nb alloys. The prior microstructure of the alloy plays a very significant role on its behavior under exposure to a hydrogen-containing environment. In the α + β Ti–6Al–4V alloy the main mechanism of hydrogen cracking is the formation and rupture of brittle titanium hydride phases. Equilibrium solid solution hydrogen solubility in the α phase is extremely small, particularly at room temperature, resulting in the formation of a potentially embrittling titanium hydride phase. In addition, due to a more rapid diffusion transport of hydrogen in the bcc β phase, the severity of hydrogen degradation in the Ti–6Al–4V alloy depends on the amount and distribution of the β phase in the microstructure. On the other hand, the Timetal Beta-21S β alloy, exposed to the electrochemical (high fugacity) hydrogen environment at room temperature, exhibits a fair resistance to hydrogen. In the refractory Ti–20 wt.%Nb alloy, hydrogen-induced second phases phenomena was observed, with the formation of a (Ti,Nb)H_x hydride in the electrochemically charged alloy and the δ Ti-hydride in the gas-phase charged alloy. These hydrogen-induced phase transitions were followed by an interesting softening effect in the Ti–20 wt.%Nb alloy, irrespective of the charging procedure.

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