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Journal of Alloys and Compounds 404–406 (2005) 613–616

Journal of ALLOYS AND COMPOUNDS

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High fugacity hydrogen effects at room temperature in titanium based alloys

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Received 3 June 2004; received in revised form 8 December 2004; accepted 15 December 2004
Available online 14 July 2005

Abstract

Titanium based alloys are ranked among the most important advanced materials for a variety of technological applications, due to their combination of a high strength/weight ratio and good corrosion behavior. However, in many of these technological applications, this alloy is exposed to environments which can act as sources of hydrogen, and severe problems may arise based on its susceptibility to hydrogen embrittlement. Both the severity and the extent of the hydrogen interaction with titanium based alloys are directly related to the temperature. Therefore, a comprehensive knowledge of hydrogen effects at room temperature in titanium based alloys will assist in determining the reliable use of these alloys in direct contact with ambient-temperature hydrogen-containing environments. The objective of this paper is to better understand the combined role of microstructure and room-temperature high fugacity hydrogen on titanium based alloys. The paper deals in detail on the effect of hydrogen at room temperature in the Ti–6Al–4V alloy, thermo-mechanically treated to a duplex and a fully lamellar microstructure. Hydrogen effects on the microstructure are studied using X-ray diffraction and electron microscopy, while the absorption and desorption characteristics are determined, respectively, by means of a hydrogen determinator and thermal desorption spectroscopy. Preliminary results at room temperature revealed hydrogen-induced straining and expansion of the lattice parameters in both alloys, at low-to-moderated hydrogen concentrations. With the increase in hydrogen content, in both duplex and fully lamellar Ti–6Al–4V alloy, cracking and second phases formation (hydrides) were observed. The main characteristics of hydrogen absorption/desorption behavior, as well as hydrogen-induced microstructural changes in both microstructures are discussed in detail.

Keywords: Hydrogen embrittlement; Ti–6Al–4V; Titanium hydrides; Absorption; Desorption; Thermal desorption spectroscopy (TDS)

1. Introduction

Titanium based alloys are ranked among the most important advanced materials for a variety of technological applications, due to their combination of a high strength/weight ratio and good corrosion behavior. However, in many of these technological applications, problems may when hydrogen comes in contact with titanium based alloys [1,2]. Unlike most other common structural materials, hydrogen has a greater solid solution solubility in titanium at low temperatures than at high. Consequently, hydrogen will tend to move down a temperature gradient and concentrate at the lowest temperature [1,3]. Although hydrogen transport is slow at low temperatures, it will occur more rapidly in the relatively open bcc lattice structure of the beta phase than in the more closed hcp lattice of the alpha phase [4]. The objective of this paper is to better understand the combined role of microstructure and room-temperature high fugacity hydrogen on titanium based alloys. The paper deals in detail on the effect of hydrogen at room temperature in the Ti–6Al–4V alloy, thermo-mechanically treated to a duplex and a fully lamellar microstructures. The main characteristics of hydrogen absorption/desorption behavior, as well as hydrogen-induced microstructural changes in both microstructures are discussed in detail.

2. Experimental

The titanium alloy used for this study was Ti–6Al–4V, thermo-mechanically treated in two microstructural

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doi:10.1016/j.jallcom.2004.12.172

conditions, duplex and fully lamellar microstructure, as described in detail elsewhere [5]. Prior to hydrogen exposure, 5 mm × 5 mm × 1 mm samples were cut from alloys plates, and were mechanically polished up to 0.05 μm. The specimens were exposed to electrochemical hydrogen charging at room temperature, in a H_3PO_4:glycerine (1:2, v/v) electrolyte, using a constant current density of 50 mA/cm^2, for different charging times. 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). The absorption and desorption characteristics are determined respectively by means of a LECO RH-404 hydrogen determinator and thermal desorption spectroscopy (TDS), using the test protocol described elsewhere [6]. For TDS measurements, the heating rates (ramps) were 3, 5 and 7 K min^{-1}, and the temperature range was 50–700 °C, both parameters being programmed into a temperature controller.

3. Results and discussion

3.1. Absorption

The amount of hydrogen absorbed in the duplex and fully lamellar microstructures of Ti–6Al–4V alloys was measured by means of LECO analysis following electrochemical hydrogenation at room temperature, and the results are presented in Fig. 1.

From Fig. 1, it can be seen that the hydrogen content absorbed in both alloys increased with the charging time. However, hydrogen uptake in the fully lamellar alloy is higher than that in the duplex microstructure. The rate of hydrogen diffusion is reported to be higher by several orders of magnitude in the β phase than in the α phase [7]. The fully lamellar microstructure exhibits a more continuous β phase, which explains the higher hydrogen uptake in comparison to microstructures with discontinuous β, such as the fine equiaxed α in the duplex alloy.

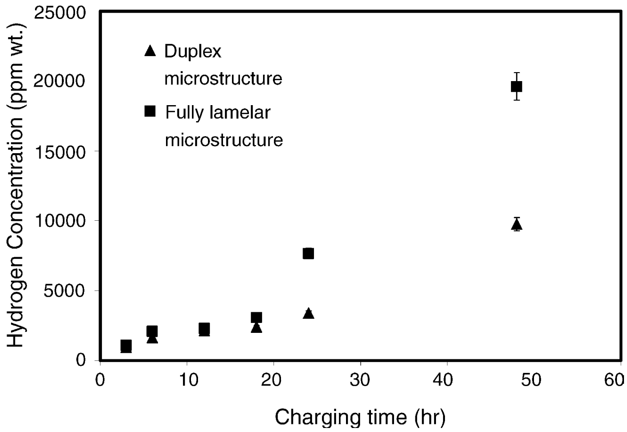

Fig. 1. Kinetics of room-temperature electrochemical hydrogen charging of duplex and fully lamellar Ti–6Al–4V specimens.

3.2. The effect of room-temperature hydrogen on the microstructure

The effect of hydrogen on the microstructure of both duplex and fully lamellar Ti–6Al–4V alloys was investigated by means of X-ray diffraction and scanning electron microscopy (SEM). X-ray diffraction patterns of the specimens, hydrogenated at 50 mA/cm^2, in H_3PO_4:glycerine (1:2, v/v) electrolyte, are shown in Fig. 2. The XRD patterns of the duplex and fully lamellar uncharged specimens exhibit very different relative peak heights, which indicates that the fully lamellar sample appears to be highly oriented due to its characteristic microstructure, in comparison to the duplex microstructure consisting of only 40% of lamellar grains of secondary α (transformed β) embedded in a 60% equiaxed matrix of primary α. The preferred orientation plane is from the $\{h\,0\,l\}$ family, since the highest peaks are of the $\{1\,0\,1\}$, $\{1\,0\,2\}$ and $\{1\,0\,3\}$ α-Ti. XRD microstructure observations of both alloys after hydrogenation for 12 h revealed that the presence of hydrogen in solid solution in both alpha and beta phases resulted in lattice expansions, as well as the precipitation of tetragonal γ-TiH. When increasing the hydrogen concentration (after 48 h of charging), in both specimens another type

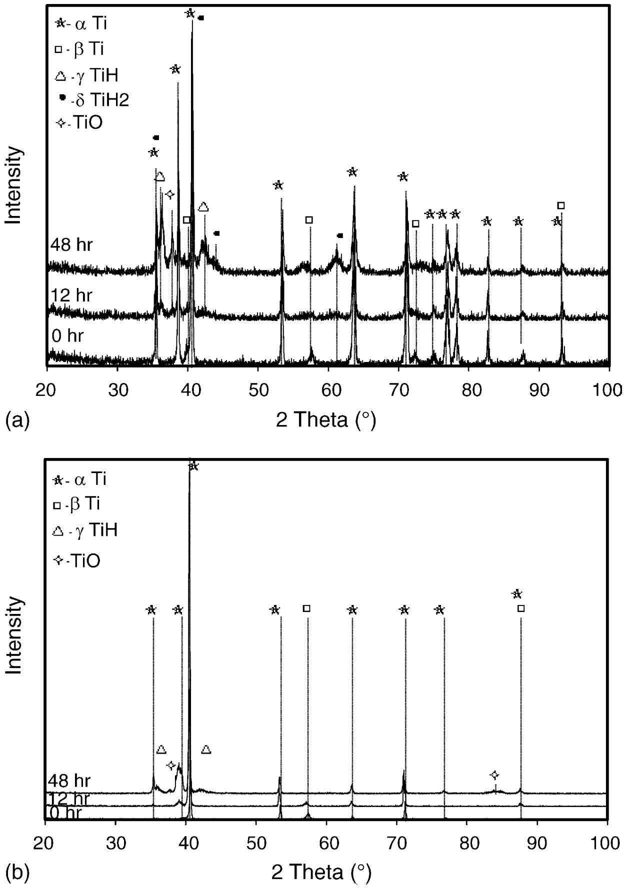

Fig. 2. X-ray diffraction patterns of uncharged and electrochemically hydrogenated at room temperature (a) duplex and (b) fully lamellar Ti–6Al–4V specimens.

of hydride, tetragonal δ-TiH_x, is formed in addition, accompanied with a small fraction of titanium oxide. It has been frequently reported [8–10] that the δ-hydride would precipitate in the alpha phase matrix when the stoichiometric ratio of the δ-hydride is less than 1.56. The co-existing α phase could be the solid solution of hydrogen in α-titanium (hcp structure). Once the hydrogen content is over the critical value of 1.56, a single phase δ-hydride-TiH_x, with x ranging from 1.56 to 1.89 would be observed. However, in comparison to the fully lamellar alloy, in the duplex material, the δ-TiH_x formed even at lower hydrogen concentrations (12 h of charging, leading to approximately 1000 ppm hydrogen), while at higher hydrogen concentrations (48 h of charging), the intensity of the hydride peaks increased significantly indicating a probable increase in the amount of the hydride phases. The precipitation of hydrides in the duplex-annealed alloy at lower hydrogen concentrations is related to the lower solubility of hydrogen in the α phase [11], especially at low temperatures, in comparison to the high terminal hydrogen solubility observed in the β phase [12].

SEM investigation revealed micro-cracks and pitting, followed with oxygen contamination in the hydrogen-attacked areas in both alloys at high hydrogen concentrations (after 48 h of charging). In the duplex microstructure, the micro-cracks were located mainly in the equiaxed grains of primary α, rather than in the β-transformed lamellar grains.

3.3. Desorption

Characteristics of hydrogen desorption were investigated by thermal desorption spectroscopy (TDS). Fig. 3 presents the TDS plots of these alloys, charged with almost the same amount of hydrogen. Note that the charging times used to receive an almost equal hydrogen concentration are different for the two alloys, due to different hydrogen absorption characteristics, discussed previously.

TDS graphs of both alloys exhibit one main desorption peak at elevated temperatures (above 550 °C). However, hydrogen desorption from β-annealed alloy occurred at higher temperatures, indicating a stronger trapping state (see Table 1). The difference in the desorption peak temperatures reveals that hydrogen is trapped in different trapping sites in these alloys.

As expected, at higher absorbed hydrogen contents, the amount of desorbed hydrogen, calculated by integration of the TDS graphs, is also higher in both alloys. From Fig. 3 and Table 1 it can clearly be seen that at relatively low hydrogen concentrations (∼1000 ppm), the amount of desorbed hydrogen is higher in the β-annealed alloy, while at higher hydrogen concentrations (∼3000 ppm) the opposite occurs. This phenomenon can be explained by the different trapping sites existing in these alloys, which may lead to different desorption mechanisms. A possible trap site might be provided by the α/β interfaces, as noted by Young and Scully [13]. Therefore, an important parameter which should be taken under consideration is the different microstructure of the alloys. The duplex microstructure is characterized by a discontinuous β phase because of the combination between equiaxed primary α grains and lamellar β-transformed grains. In comparison, the fully lamellar microstructure exhibits a more continuous β phase, thus, more α/β interfaces. Thus, in the β-annealed alloy, hydrogen desorption is probably related to the α/β interfaces, which act as a strong trapping site, leading to

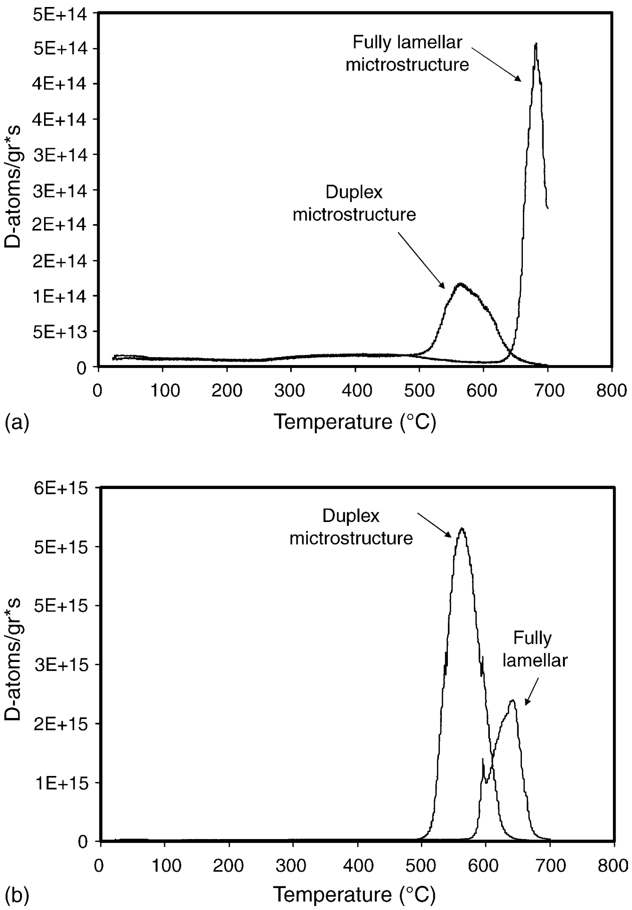

Fig. 3. TDS plots of duplex annealed and β-annealed Ti–6Al–4V alloys, charged cathodically up to almost equal hydrogen concentrations of (a) approximately 1000 ppm and (b) approximately 3000 ppm.

Table 1
Parameters of hydrogen desorption from duplex and fully lamellar Ti–6Al–4V specimens, hydrogenated electrochemically at room temperature

Ti–6Al–4V alloy's microstructure	Hydrogenated up to ∼1000 ppm		Hydrogenated up to ∼3000 ppm	
	Peak temperature (°C)	C_H desorbed (mole H/ mole M)	Peak temperature (°C)	C_H desorbed (mole H/ mole M)
Duplex	562	1.51×10^{-4}	562	3.37×10^{-3}
Fully lamellar	682	1.91×10^{-4}	642	1.11×10^{-3}

a higher desorption temperature (642–682 °C). On the other hand, we assume that in the duplex specimen, hydrogen desorption could be related to titanium hydrides dissociation at the elevated temperature of 562 °C. This might explain the higher amount of desorbed hydrogen at ∼3000 ppm, since at higher hydrogen concentrations, X-ray diffraction patterns revealed a probable increase in the amount of hydride phases in the duplex-annealed alloy.

4. Conclusions

In this work, the effects of room-temperature high fugacity hydrogen in Ti–6Al–4V alloy were investigated, with specific emphasis on the role of microstructure in the absorption/desorption behavior and the interactions between hydrogen atoms and the possible trap sites in this alloy. The conclusions obtained are summarized as follows:

(i) Hydrogen concentrations absorbed in both duplex and fully lamellar Ti–6Al–4Valloys increased with the charging time. However, hydrogen uptake is higher in the fully lamellar alloy.

(ii) Hydrogen induced strain in both alloys by increasing their lattice parameters, expanding their cell volumes and leading to second phases (hydrides) precipitation. However, due to the lower solubility of hydrogen in the α phase, hydrides precipitation in the alloy with a duplex microstructure occurred at lower hydrogen concentrations.

(iii) TDS graphs of both alloys exhibit one main desorption peak at elevated temperatures (above 550 °C). However, hydrogen desorption from the fully lamellar alloy occurred at higher temperatures. At relatively low absorbed hydrogen concentrations (∼1000 ppm), the amount of desorbed hydrogen is higher in the fully lamellar alloy, while at higher hydrogen concentrations (∼3000 ppm) the opposite occurs. This phenomenon can be explained by the different trapping sites existing in these alloys due to the different microstructural features and morphology (fully lamellar versus duplex-microstructure), and the different hydrogen ability to form second phases (hydrides), which may lead to different desorption behavior.

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