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Mechanical and microstructural changes of Ti and Ti–6Al–4V alloy induced by the absorption and desorption of hydrogen

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Abstract

Vickers microhardness tests and X-ray diffraction analysis (XRD) were used to study the mechanical and the structural properties of Ti and the Ti–6Al–4V alloy during the hydrogen absorption–desorption process. Ti and the Ti–6Al–4V alloy were hydrogenated at different temperatures (150, 300, 450, 500, 550, 600, 650 and 750 °C), reaching maximum hydrogen concentration of $(2.95 \pm 0.24) \times 10^{22}$ H/cm^3 for Ti and $(2.82 \pm 0.22) \times 10^{22}$ H/cm^3 for the alloy. Hardness of both metals increased with hydrogen absorption, but a decrease in the Vickers microhardness number was observed in both materials when they started to loose hydrogen. The XRD analysis showed changes in the crystal size in those samples with large amounts of hydrogen, as well as changes in crystal orientation in the Ti–6Al–4V alloy induced by the hydrogen absorption.

Keywords: Metal hydride; Hydrogen absorption materials; Rutherford backscattering; X-ray diffraction

1. Introduction

Metals, such as $LaNi_5$, Mg_2Ni, ZrV_2, TiFe, Ti and Ti–6Al–4V are good candidates for industrial and medical applications. These metals have been considered to be good hydrogen storage materials because they absorb and release hydrogen in large amounts without the deterioration of their structure [1]. Ti and the Ti–6Al–4V alloy have also been used for surgical implants due to their excellent corrosion resistance as well as their biocompatibility. In order to improve the hardness properties of Ti and the Ti–6Al–4V alloy, the introduction of hydrogen into the metal or the implantation of certain types of ions have been carried out. When metallic ions are implanted into the material, they remain inside it producing a stable material structure, but hydrogen can leave the material while the metal is kept stored at room temperature, modifying the hardness surface properties of the metal.

In this work, Vickers microhardness tests and X-ray diffraction analysis are used in order to study the mechanical and structural stability of Ti and the Ti–6Al–4V alloy materials during different stages of the hydrogenation–dehydrogenation process.

In a previous work [2], we reported that Ti and Ti–6Al–4V alloy samples were hydrogenated during 2 h in a 50% hydrogen and 50% argon atmosphere, 1 atm pressure and a flux of 50 cc/min, each one. These samples were heated at different temperatures (150, 300, 450, 500, 550, 600, 650 and 750 °C) during the hydrogenation process in order to increase the hydrogen absorption. The hydrogen concentrations were measured by using the Elastic Recoil Detection Analysis (ERDA) technique at 3 MeV. We found that the hydrogen absorption started around 550 °C for Ti and the Ti–6Al–4V alloy, reaching maximum concentrations of $(2.95 \pm 0.24) \times 10^{22}$ H/cm^3 at 650 °C and $(2.82 \pm 0.22) \times 10^{22}$ H/cm^3 at 750 °C, respectively, as can be seen in Fig. 1. The ERDA measure that corresponds to the Ti sample hydrogenated at 750 °C is not presented in this figure since the sample cracked during the hydrogenation process, which made it impossible to measure its hydrogen content, surface oxidation, microhardness value or diffraction pattern.

We also reported in reference [2], a subsequent loss of hydrogen in all the samples of Ti and the Ti–6Al–4V alloy after several months of being kept stored at room temperature. Differences in mechanical strength between Ti and the Ti–6Al–4V alloy related to 750 °C hydrogenation temperature were also reported. While

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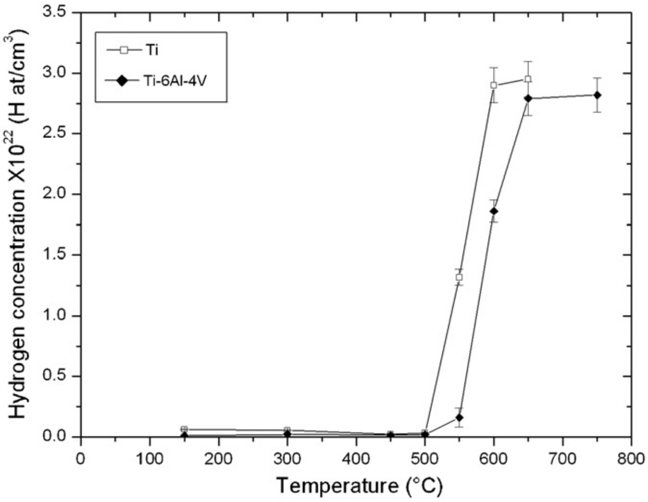

Fig. 1. Hydrogen concentration versus hydrogenation temperature for the Ti and the Ti–6Al–4V alloy samples. The hydrogen absorption starts around 550 °C for both materials.

the Ti–6Al–4V alloy was hydrogenated at this temperature with no evident structural damage, the Ti structure became brittle and the material cracked when it reached 750 °C.

Hardness (H) is defined as the ratio of the applied load P to the resulting indentation area A. The relation to obtain the Vickers microhardness (H_V) is

$$H_V = 1854\frac{P}{d^2} \tag{1}$$

The Vickers microhardness test involves a simple indentation by loading a well-known weight square-based diamond pyramid, with an angle of 136° between the opposite faces. Afterward the lengths of the diagonals (d) are measured in order to obtain the surface area of the indentation. The harder the material, the smaller the indentation for a given load. As the indentation is extremely small, the Vickers test involves the use of a microscope as a tool to measure the indentation length [3,4].

2. Experimental

The Ti samples, manufactured by Goodfellow, are 99.6% purity and consisted of slices cut from 9.5 mm diameter rods. Some Al, Cr, Mn, Ni and V impurities were present in the metal at 500 ppm. The Ti–6Al–4V alloy samples, also manufactured by Goodfellow, were similarly cut from 10.0 mm diameter rods, being 650 ppm of oxygen the maximum impurity. After cutting they were polished on diamond pastes and cloths down to 0.5 μm finish. Afterwards each sample was hydrogenated in a 50% hydrogen and 50% argon atmosphere, at 1 atm pressure and a flux of 50 cm^3/min during 2 h. The temperatures of the heat processes were in the interval 150–750 °C for both materials.

A static microhardness tester model MHT-2 from Matsuzawa Seiki was used to measure the Vickers microhardness of Ti and the Ti–6Al–4V alloy samples. The test loads used for all the samples during the study were 50, 100, 200 and 300 g and the load holding time was 15 s. For each load the mean of the diagonal length of each sample was calculated from ten indentations. The Vickers microhardness value was obtained by using Eq. (1). The samples were identified by their hydrogenation temperature (150, 300, 450, 500, 550, 600, 650 and 750 °C) and they were measured in three different stages of the hydrogenation–dehydrogantion process. The first measure was carried out immediately after the metals were hydrogenated, while the second and third measurements were done 4 and 10 months after the hydrogenation took place. Conventional X-ray diffraction was performed at the Instituto de Investigaciones en Materiales, UNAM with a Bruker-axs D-8 ADVANCE diffractometer, using the Cu Kα radiation.

3. Results and discussion

Vickers microhardness test carried out on both materials showed that the mechanical properties of the materials are modified when hydrogen is absorbed by showing a tendency of the material to become harder when hydrogen amount increases. It was also observed an ISE normal behavior in both materials that can be the result of a surface effect due to the hydrogenation process in the samples, where a small oxide layer is formed in the metal surface that produce an increase in the hardness of the surface in both materials. The presence of the oxide layer was confirmed by the Rutherford Backscattering Spectrometry (RBS) using the elastic scattering resonance $^{16}O(\alpha, \alpha)^{16}O$ at 6.585 MeV, that is 80 times larger than its corresponding Rutherford cross-section, This scattering resonance was used in order to obtain high sensitivity in the oxygen measurement.

A decreasing in the hardness value with time was observed in all the hydrogenated samples, independently on the material or the hydrogen concentration. This behavior can be seen in Fig. 2, which corresponds to the Ti–6Al–4V alloy with an initial hydrogen concentration of $(1.86 \pm 0.15) \times 10^{22}$ H/cm^3. The reduction of microhardness can be understood in terms of the release of hydrogen with time, reported in reference [2]. The curves plotted in Fig. 2 represent the Meyer's curves of the Ti–6Al–4V alloy sample hydrogenated at 600 °C, as well as the Ti–6Al–4V alloy reference sample, with any hydrogenation process. The first measure was carried out immediately after the sample was hydrogenated. After that, the sample was kept stored at room temperature and it started to loose hydrogen in a "natural way". We mean as "natural way" as the process by which the mate-

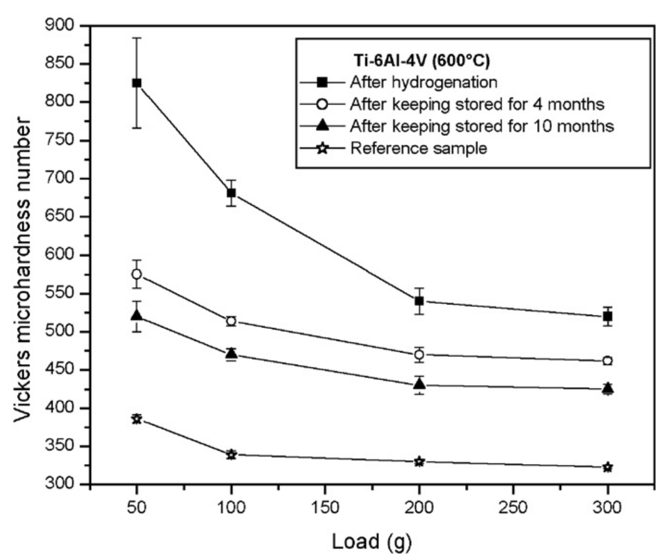

Fig. 2. Vickers Microhardness measures for the Ti–6Al–4V alloy sample hydrogenated at 600 °C. The difference in the curves can be explained due to the hydrogen lost during the 4 and 10 months that the sample was kept stored at room temperature. The reference sample corresponds to the hardness measurement made to the Ti–6Al–4V sample before the hydrogenation process took place. The material's hardness is directly related with its hydrogen concentration.