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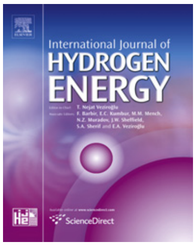

Influence of surface roughness on consecutively hydrogen absorption cycles in Ti–6Al–4V alloy

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ABSTRACT

In the present work the influence of roughness of the material surface with hydrogen absorption in Ti–6Al–4V alloy during four hydrogenated cycles is studied. The Ti–6Al–4V alloy samples were hydrogenated during several cycles at 650 °C for two hours, in 50% hydrogen and 50% argon atmospheres, 1 atm pressure and a flux of 50 cm^3/min each one. The hydrogen concentrations are measured using Elastic Recoil Detection Analysis technique; meanwhile the roughness is measured using an Atomic Force Microscope. X-ray Diffraction analysis shows changes in crystal orientation due to hydrogen absorption. The hydrogen capacity of the Ti–6Al–4V alloy is observed to be directly correlated to the surface quality of the sample during the first hydrogenation cycles, but in the fourth cycle, the hydrogen absorption is almost equal for all the samples independently of their surface roughness.

1. Introduction

Metal hydrides have been used for storage of hydrogen due to their large capacity to accommodate an extremely high density of hydrogen in their structures [1]. It is possible to pack more hydrogen into a metal hydride than into the same volume of liquid hydrogen because when a metal that forms a hydride is brought in contact with gaseous hydrogen, the hydrogen molecules are adsorbed onto the surface of the material. If enough energy is given to the system, the hydrogen molecules can dissociate into hydrogen atoms, which tend to enter to the crystal lattice of the metal and occupy interstitial sites. As the energy given to the system increases, hydrogen atoms are forced into the crystal until the metal becomes saturated with hydrogen. At this stage, the material goes into a new phase: the metal hydride, which allows the material to absorb hydrogen in larger amounts. In a previous work [2] it was observed that hydrogen is not absorbed in the Ti–6Al–4V until a threshold temperature is reached. In that work a 600 °C temperature was measured to be the minimal energy needed to dissociate the hydrogen molecule during the absorption process. This minimal temperature is necessary when the experimental conditions are similar as the ones used in this work [2]. In other cases, as when working in a vacuum system, this threshold temperature must be different.

Some titanium alloys have attracted interest for storage of hydrogen because they absorb and release hydrogen in large amounts without the deterioration of their structures [1,3–5]. Although some techniques, such as SPS [6] or the use of catalysts process [7], have been developed in order to prepare the best material that will be able to improve the hydrogen storage capacities, bulk materials as the one used in this work are also good candidates for hydrogen storage. Ti–6Al–4V alloy is composed by a biphasic structure: the beta phase (BCC structure) surrounding the alpha phase (HCP structure). The fact that the alloy has a BCC structure makes easier the hydrogen absorption, due to the way hydrogen atoms enter

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the crystalline structure and fit in the interstitial sites of the crystal. In the case of the beta phase of the Ti–6Al–4V alloy, the BCC structure has 6 octahedral sites and 12 tetrahedral sites per unit cell where hydrogen can fit. The octahedral and tetrahedral sites in a BCC structure are 3 times more than the ones found in the HCP and FCC lattices [8,9]. It has been also observed that the rate of hydrogen diffusion in a BCC structure is several orders of magnitude higher than in an HCP or an FCC structure [10].

The initial steps of hydrogen absorption not only depend on the crystalline structure, but also of the quality of the surface of the metal or alloy. A combination of metal oxides and hydroxides on the metal surface can act as a diffusion barrier reducing the uptake rate of hydrogen [11]. Heat treatment is used to remove the oxygen atoms from surface and dissolve them into the bulk, leaving fresh metal surfaces and improving hydrogen absorption. This is the reason that accurate measurements of oxygen and hydrogen content in the material must be conducted, in order to correlate the sample oxidation with the hydrogen storage capacity. There are several methods used to detect oxygen and hydrogen in metallic structures, but they have limited applications for the determination of concentration and depth profiles. Another limitation of these methods is that they are destructive, in contrast to the Ion Beam Analysis Techniques, such as Elastic Recoil Detection Analysis (ERDA) [12] and Rutherford Backscattering Spectrometry (RBS) [13] which give a very precise measurement of the concentration of hydrogen and oxygen, respectively. In both techniques, a beam of collimated and monoenergetic particles generated by an accelerator collide with the sample. Particles are scattered out of the target and reach a silicon surface barrier detector where they are analyzed. The analog signals that leave this system are processed by a multichannel analyzer to form the RBS and ERDA spectra. In these methods the element to be analyzed is identified by the energy and type of the emitted particles coming from a specific reaction between the incident ion and the given target element. The main difference between RBS and ERDA is that in the first technique the incident ion and the scattered particle are the same (α-particles), whereas in the second case the incident ion (α-particles) and the detected recoil ion (hydrogen) are different.

2. Material and methods

Ti–6Al–4V samples manufactured by Goodfellow were 99.6% purity. The samples consisted of 7 mm thick slices cut from 10.0 mm diameter rods which were annealed in argon at 675 °C by the manufacturer. After cutting, and in order to obtain samples with different surface quality, they were polished using Emery paper with different grit range between Nos. 600 and 2500 and diamond paste of 3, 1 and 0.5 μm used on a cloth to produce a scratch-free mirror finish. Afterwards, the samples were hydrogenated at 650 °C in a 50% hydrogen and 50% argon atmosphere, at 1 atm pressure, and a flux of 50 cm^3/min, during two hours. The mixture of gases (H_2/Ar) is used for security in the system during the hydrogenation process; nevertheless Filimonov et al. [1] showed in their work that a flow of Ar or He plays an important role during absorption and desorption of hydrogen. More detailed studies using the experimental conditions (temperature, gas fluxes, etc) of this work have to be conducted in this sense in order to confirm this result.

The samples were labeled depending on their surface quality, which also depends on the different grit range used during the polishing process. Table 1 shows the polishing characteristics of each sample and the way they have been labeled though the work.

The amounts of oxygen and hydrogen in the metals were obtained using RBS and ERDA, respectively. Four hydrogenation cycles were conducted to the samples in order to study the correlation between consecutively hydrogen absorption with surface quality. The samples were hydrogenated every two months and after this process, their hydrogen content was measured. It is important to perform these measurements immediately after the hydrogenation process in order to prevent the lost of hydrogen during the storage; because it has been observed in other works [2] that hydrogen is released from the alloy while the sample had kept stored at room temperature. After the hydrogen amounts were measured, the samples were kept stored for two months at room temperature until the next hydrogenation took place. Before each hydrogenation cycle, the oxygen concentration was measured in order to quantify the surface oxide layer of the samples that would be hydrogenated.

During the RBS study, a collimated 6.585 MeV α-particle beam was used to measure the amount of oxygen in the samples. The alpha particles were obtained using the Instituto de Física 3MV 9SDH-2 Pelletron accelerator, meanwhile the projectiles scattered at 167° were detected with a surface barrier detector. Even though RBS has been extensively used for ion beam analysis at 2 MeV, in many cases it is ineffective for light element analysis due to overlapping signals, so if sensitivity must be improved, higher incident energy must be used. When raising the incident energy, the scattering cross section may become non-Rutherford [14] and may exhibit large resonances. These resonances are regions where the scattering cross section is greatly enhanced over the Rutherford cross section at the same energy and are very useful for measuring elements such as the oxygen [15]. One of the oxygen resonances is presented at 6.585 MeV and enhances the oxygen signal by 80 times, so even a small amount of oxygen can be detected using RBS.

In order to measure the hydrogen concentration, the samples were irradiated with a collimated 3 MeV α-particle using the same Pelletron accelerator as in the case of the RBS

Table 1 – Polishing characteristics of the samples.

Sample	Emery paper			Diamond paste 3 μm, 1 μm, 0.5 μm
	No. 600	No. 1500	No. 2500	
S-1	×			
S-2	×	×		
S-3	×	×	×	
S-4	×	×	×	×