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# Effect of Absorption and Desorption of Hydrogen in Ti and Ti Alloys

Alejandra López-Suárez

**Abstract**

A study of the hydrogen (H) storage capacity of pure Ti and the Ti-6Al-4V alloy is presented. The importance of an accurate quantification of oxygen and hydrogen in the materials used for hydrogen storage, the activation process and the cyclic hydrogenations, the effect of surface quality during hydrogen uptake, the improvement of hydrogen absorption using ion irradiation, and the hydrogen desorption are some topics discussed in this chapter.

**Keywords:** metal hydrides, hydrogen storage, absorption, desorption, Ti, Ti-6Al-4V, ERDA, RBS

## 1. Introduction

The history of civilization in terms of energy goes from the use of wood and coal to the use of oil and natural gas. By mid-twentieth century, oil became the world leader in the energy field. Notwithstanding the great advantages of the hydrocarbon fuel, it is a non-renewable fossil resource, which is running out and its extraction is becoming more expensive. Besides, their excessive use has led to serious problems of global pollution, which have brought severe climate change on Earth. For this reason, the next step in the energy scale could be the hydrogen (H).

Hydrogen is the most abundant element in nature and can be used as fuel in liquid or gaseous form, but its storage is risky and expensive. However, these drawbacks hydrogen has an alternative solution for storage: metal hydrides (MH), which are chemical compounds formed by a metal (M) and hydrogen (H). One of the main advantages of the use of metal hydrides as energy sources is that unlike the non-renewable ones, they do not cause pollution when

burned, because its by-product is water. For this reason, hydrogen can be considered as a clean fuel.

Hydrogen can be stored in fuel cells to produce electricity and can be used in applications as diverse as transportation or electronics industry in batteries for laptops and cell phones applications. Undoubtedly, one of the most important challenges that the hydrogen-based economy has is its storing. In order to use hydrogen as a fuel, it needs to be safely stored in a medium that allows absorption, storage, and desorption, besides an easy transport. There are several ways of storing hydrogen, among them are metal hydrides, hydrides ceramics, carbon-based materials, etc.

As a consequence of the so called "Oil Crisis," in the 1970s, metal hydrides started to be considered as good candidates for using in hydrogen energy storage, due to their large capacity to accommodate an extremely high density of hydrogen in their structures. It is possible to pack more hydrogen into a metal hydride than into the same volume of liquid. The reason is that 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.

## 2. Metal hydrides for hydrogen storage

Metal hydrides, such as palladium, zirconium, or titanium, form an important group of reversible-sorbing materials. The main advantage of metal hydrides over other hydrogen storage media, such as activated carbon, carbon nanotubes, or zeolites, is that they can be reversible hydride, and they can also release hydrogen of the metal hydrides in an extremely pure way, which is an important factor when considering hydrogen for mobile applications [1].

The process of hydrogen absorption (or desorption) by metals is reversible and involves the surface and the bulk of the material, through several steps. In the gas phase, the reaction involves the following mechanism:

**1.** Surface physisorption (desorption) of molecular hydrogen ($H_2$). In this step, the hydrogen molecules adsorb (desorb) at (from) the surface of the metal (M).

$$M + H_2 \leftrightarrow M - H_2$$
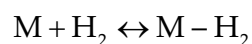
**2.** Surface dissociative chemisorption (recombination). This leads to the formation (desorption) of atomic hydrogen at the surface of the metal.
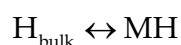
$$2M - H_2 \leftrightarrow 2M - H$$
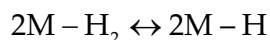
**3.** Surface absorption (desorption). During this step, the adsorbed atomic hydrogen is absorbed (desorbed) by (from) the metal in its sub-surface.

$$H_{ad} \leftrightarrow H_{ab}$$
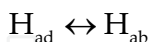
**4.** Diffusion. The atomic hydrogen is transported from subsurface to the bulk region.

$$H_{sub} \leftrightarrow H_{bulk}$$

**5.** Phase transformation. Leads to the precipitation (dissolution) of the metal hydride phase.

$$H_{bulk} \leftrightarrow MH$$

Pure titanium is considered to be an element with a high affinity to hydrogen; however, high temperature has to be used in order to absorb hydrogen in this material [2]. To avoid this inconvenience, some titanium alloys, such as TiFe, $Ti_2Ni$, $TiMn_2$, or Ti-6Al-4V, have attracted interest for storage hydrogen because they can absorb and release hydrogen in large amounts and at lower temperature than pure titanium.

The maximum hydrogen capacity of the material depends on the number of hydrogen sites that are available for hydrogen occupation. For instance, the Ti-6Al-4V alloy is composed by a biphasic structure: the beta phase (Body-centered cubic –BCC-structure) surrounding the alpha phase [hexagonal closed packed (HCP) structure]. The fact that this alloy has a BCC structure eases the hydrogen absorption, due to the way hydrogen atoms enter 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 three times more than the ones found in the HCP and face-centered cubic (FCC) lattices [3]. It has also been observed that the rate of hydrogen diffusion in a BCC structure is several orders of magnitude higher than in a HCP or a FCC structure [4]. **Figure 1** shows the scanning electronic microscopy (SEM) micrographs of (a) pure titanium and (b) the Ti-6Al-4V alloy. Pure titanium has a hexagonal closed packed (HCP) crystalline structure; meanwhile, the Ti-6Al-4V alloy shows an alpha phase (HCP) composed by Ti and Al, which looks as a dark zone in **Figure 1b**, surrounded by the beta phase (BCC) composed by Ti and V.

## 2.1. The importance of an accurate quantification of oxygen and hydrogen in the materials used for hydrogen storage

The initial mechanisms of hydrogen absorption depend on the crystalline structure of the metal, but also on its surface quality. The uptake rate of hydrogen can be reduced by a combination of metal oxides and hydroxides on the metal surface, acting as a diffusion barrier [5]. In this way, accurate oxygen and hydrogen measurements must be conducted in order to

correlate the storage capacity of the metal with sample oxidation. In the literature, several techniques are used to detect oxygen and hydrogen in materials; nevertheless, these methods are destructive and have limitations for the determination of concentrations and depth profiles. The ion beam analysis (IBA) techniques, such as Rutherford backscattering spectrometry (RBS) [6] and elastic recoil detection analysis (ERDA) [7], are non-destructive nuclear techniques that allow performing a very accurate measurement of the concentration and depth profile of oxygen and hydrogen, respectively.
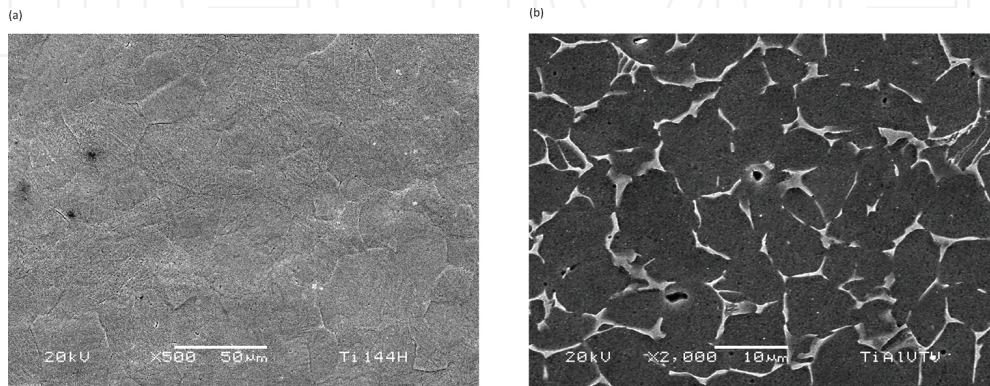


**Figure 1.** SEM micrographs of (a) pure titanium and (b) Ti-6Al-4V alloy [8].

The physical principle of RBS consists of impinging a beam of collimated and monoenergetic particles (usually light ions such as hydrogen or helium) on the material to be analyzed. As the result of the interaction, part of the energy of the incident particle is transferred to the nucleus of the atom in the sample; so that the backscattered particle contains information of the target, because the reduction in energy of the incident particle depends on the mass of the projectile and the nucleus.

The ERDA technique is used to quantify the concentration of light elements, such as hydrogen and carbon. During an ERDA experiment, a beam of collimated and monoenergetic ions heavier than those who are to be detected, impinges on a material. The projectiles collide elastically with the nuclei of the sample, and as they are lighter than the projectiles, they acquire enough energy to leave the material. Simultaneously with the light ions, heavy projectiles could leave the sample and can reach the detector. For this reason, it is essential to place an absorber of Mylar or aluminum before the detector in order to stop the heavier projectiles and only let to lighter recoils to reach it.

In both techniques, the element that will be analyzed is identified by the energy and the type of the emitted particles that comes from the RBS or the ERDA reactions.

In the case of oxygen measurements, an oxygen resonance energy must be used in order to quantify the element concentration. This is because the Rutherford cross section of the oxygen is quite low, causing its RBS signal to be veiled by the signal of other elements present in the material. Oxygen resonances are presented at different energies, being the most common the ones located at 3.045 and 6.585 MeV. These resonances increase the cross section of the element by several times, making possible to improve the oxygen signal and quantify its concentration.

In the next section, the 6.585 MeV oxygen resonance was used during the RBS experiment. This energy allowed obtaining the carbon signal as well, which is usually completely veiled by other elements.

## 2.2. The activation process and the cyclic hydrogenations

Since the metals or metal alloys used as hydrogen storage materials do not absorb hydrogen at room temperature, they must be activated. Several activation modes, including activation at high temperatures, are attempted in order to obtain a material capable to absorb hydrogen. After the thermal process, the number of paths for hydrogen to diffuse into the material increases, creating micro cracks at the grain boundaries that produces large amounts of clean surface, easing the hydrogen absorption. On the other hand, if the surface of the material is not completely clean or is covered with a surface passivation layer (combination of metal oxides and hydroxides), the material will not absorb until the contaminants or the passivation layer are removed. The activation process in this instance can also occur by increasing the temperature of the material.

The metals that were used as hydrogen storage materials in this chapter are pure titanium and the titanium alloy Ti-6Al-4V, which were manufactured by Goodfellow. The samples were polished and then were ultrasonically cleaned in acetone, followed by rinsing with deionized water. The later cleaning was used in order to remove any kind of impurity from the surface of the sample. Once the cleaning process was completed, the samples were hydrogenated in a 50% hydrogen and 50% argon atmosphere, at 1 atm pressure and a flux of 50 cc/min, during 2 h. The temperature of the hydrogenation process ranged from 150 to 650°C. When the hydride is formed during the first hydrogenation cycle, some micro-cracks are revealed in both metals, as is shown in **Figure 2** [8]. This figure shows a SEM micrograph of a Ti-6Al-4V alloy sample taken after the activation process. These micro-cracks are the result of the stress induced at the grain boundaries of both materials, since the density of the hydride is less than the metal. As a consequence of the hydrogenation reaction, the volume of the grains increases producing cracking in the grains and exposing new surfaces. This process is called the activation of the material. After activation, the particles have a higher ratio of surface area to volume than before the hydrogenation process, so the metals are able to react easily with hydrogen [9].

The activation process also reduces the metal oxides and the hydroxides deposited on the metal surface. This behavior is observed in **Figure 3**, where two RBS spectra of a Ti-6Al-4V alloy are shown before (**Figure 3a** [8]) and after (**Figure 3b**) activation. The RBS spectra show the normalized yield or number of counts of the elements present in the sample versus energy. During the RBS experiment a collimated 6.585 MeV alpha particle beam was used to measure the amount of oxygen in the samples. The 6.585 MeV oxygen resonance was used in order to improve the sensitivity of the element during the measurement. The resonances are regions where the scattering cross section is enhanced over the Rutherford cross section at the same energy and are very useful for measuring light elements, such as oxygen and carbon. After comparing the spectra of **Figure 3**, a high reduction in the oxygen concentration after activation is clearly observed. This result confirms that activation process plays an important role in cleaning the surface of the metals and preparing them for future hydrogenations.
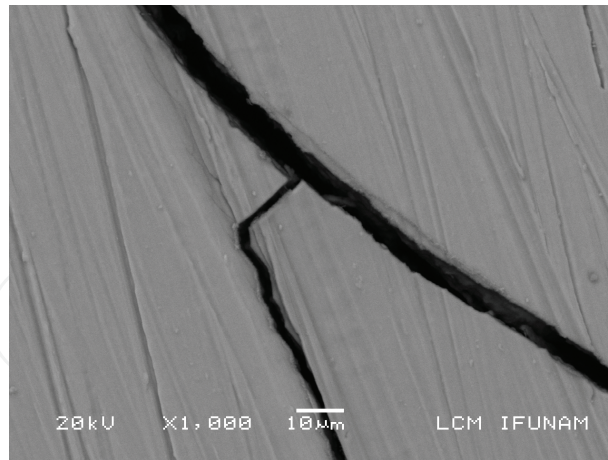
**Figure 2.** SEM micrograph of a Ti-6Al-4V alloy sample after activation [8].
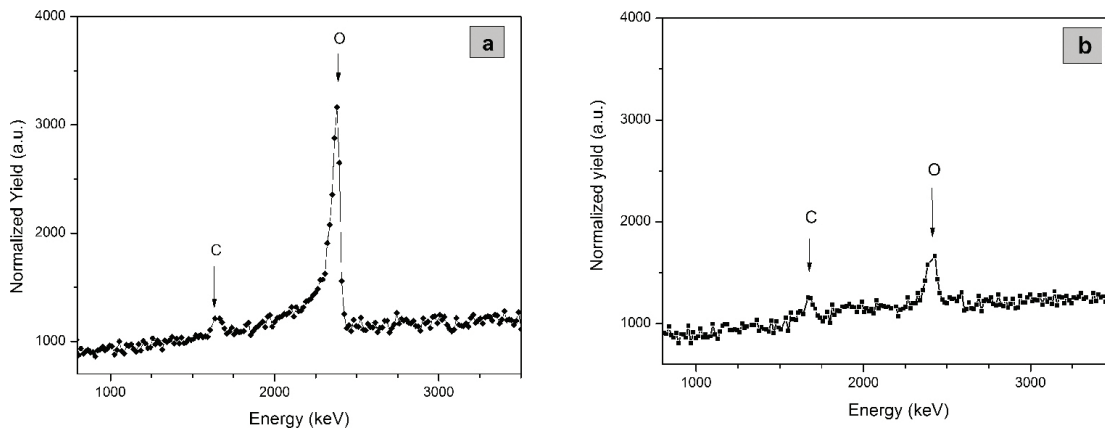


**Figure 3.** RBS spectra of Ti-6Al-4V alloy before (a) [8] and after (b) activation. The oxygen concentration is reduced considerably after the activation process.

Once the samples are activated, the hydrogen concentration is measured using the ERDA technique. In order to measure the hydrogen content, the samples were irradiated with a collimated 3 MeV alpha particle beam. The surface of the samples was placed at an angle of 15° with respect to the incoming beam; meanwhile a surface barrier detector was placed at an angle of 30° to the beam direction in order to detect the hydrogen recoils. A 12 μm Mylar foil was placed in front of the detector to stop elastically scattered ions heavier than the recoil hydrogen. Equation (1) was used to calculate the hydrogen concentration before and after the hydrogenation process. This equation relates the yield ($Y_r$) of the recoil atoms detected at channel $E_d$ with channel width $\delta E_d$, with the atomic density of the recoil hydrogen atom ($N_r$) at the depth $x$.

$$Y_r = \frac{Q N_r \sigma_r \Omega \delta E_d}{cos\theta_1 \delta E_d dE_d / dx} \tag{1}$$

where $Q$ is the incident projectile fluence, $\sigma_r$ is the recoil differential scattering cross section, $\Omega$ is the detector solid angle, and $dx$ is the increment of depth at $x$ corresponding to an increment in energy $dE_d$ and $\theta_1$ is the incident angle.

The scattering cross section is given by the equation:

$$\sigma_r = \frac{\left[ Z_1 Z_2 e^2 \left( M_1 + M_2 \right) \right]^2}{\left[ 2M_2 E_0 \right]^2 cos^3\phi} \tag{2}$$

where $Z_i$ and $M_i$ are the atomic number and the atomic mass of the $i$ element, respectively, $E_0$ is the incident energy of the projectile, and $\varphi$ is the recoil angle.

In order to study the behavior of the activation temperature in pure titanium and the titanium alloy Ti-6Al-4V, the hydrogen doping was performed at temperatures ranging from 150 to 650°C. According to Eq. (1), the hydrogen concentrations in pure titanium and the Ti-6Al-4V alloy are shown in **Figure 4** [2]. In both cases, the ERDA results show an increment in hydrogen concentration at temperatures higher than 550°C. The figure shows that hydrogen is not absorbed until a threshold temperature is reached, which is the activation temperature. In pure titanium, this threshold temperature is closed to 550°C, but in the alloy, it is located between 550 and 600°C. It is also observed in **Figure 4** that above this temperature, the hydrogen concentration reaches a value close to $3 \times 10^{22}$ H atoms/cm³ in both materials, which is the maximum concentration that the material is able to get after activation. It will be noticed later that in both materials this hydrogen concentration can easily increase during cyclic hydrogenations.
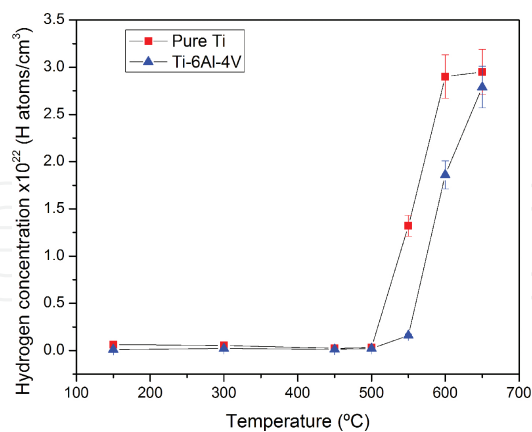


**Figure 4.** Hydrogen concentration versus hydrogenation temperature for pure Ti and the Ti-6Al-4V alloy [2].

Once the samples are activated, they can be cyclically hydrogenated in order to study the hydrogen absorption of the materials. **Figure 5** shows the ERDA spectra of a Ti-6Al-4V alloy sample hydrogenated three times after activation, where *"hydrogenation 1,"* in **Figure 5**, corresponds to the activation process. After the activation process, the samples were hydro-

genated every 2 months and after that, their hydrogen concentration was measured, as it is shown in **Figure 5**. The curve labeled as *"reference sample"* corresponds to a Ti-6Al-4V alloy with any hydrogenation process. The tiny and superficial peak that it shows is due to the hydrogen contained in the material after preparation and before the hydrogenation process. This value was subtracted from the hydrogenated curves in order to obtain an accurate hydrogen concentration. The results in this figure also show that hydrogen content increases after each hydrogenation process, which make us assume that the Ti-6Al-4V alloy can be considered a good material for hydrogen storage purposes.
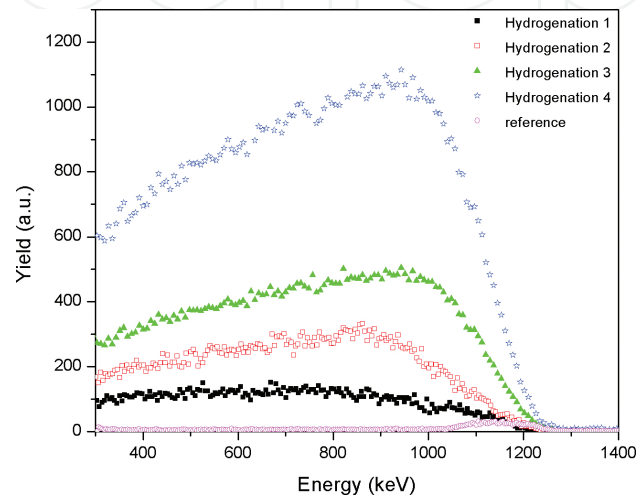


**Figure 5.** ERDA spectra of Ti-6Al-4V alloy after cyclic hydrogenations [8].

One way to compare the hydrogen storage of the materials is by means of its gravimetric storage capacity (wt%). This amount gives the percentage weight of hydrogen relative to the metal. The gravimetric storage capacity of Ti and Ti-6Al-4V alloy samples after each hydrogenation cycle was calculated by using Eq. (3).

$$wt = \frac{wt(\text{H})}{wt(\text{H+M})} \times 100 \tag{3}$$

where H and M represent the hydrogen atoms and all the metal atoms in the material, respectively.

**Table 1** shows the gravimetric storage capacity of Ti and Ti-6Al-4V alloy after cyclic hydrogenations [8]. One can appreciate that the storage capacity increases after each cycle and that after activation (first hydrogenation) the storage capacity of both materials increases considerably. After the second cycle, the increment of hydrogen in the metal and the alloy is lower, but it continues increasing. According to **Figure 2** and the titanium SEM micrographs not presented in this chapter, we can assure that after activation, both materials present microcracks that ease the hydrogen diffusion through the materials, increasing the storage capacity after each hydrogenation cycle.

| Hydrogenation cycle | Gravimetric storage capacity wt% (Ti) | Gravimetric storage capacity wt% (Ti-6Al-4V) |
|---|---|---|
| First (activation) | $3.02 \pm 0.21$ | $2.93 \pm 0.20$ |
| Second | $3.39 \pm 0.23$ | $3.46 \pm 0.24$ |
| Third | $3.49 \pm 0.24$ | $3.55 \pm 0.25$ |
| Fourth | $3.61 \pm 0.25$ | $3.64 \pm 0.25$ |

**Table 1.** Gravimetric storage capacity of Ti and Ti-6Al-4V after cyclic hydrogenations [8].

On the other hand, **Table 2** presents the gravimetric storage capacity of some other materials used as hydrogen storage media [10]. According to the data of **Table 2**, the storage capacity of our materials after the fourth hydrogenation, has similar values to those materials that are commercially used as hydrogen storage materials. This fact makes us think that pure titanium and the Ti-6Al-4V alloy are good candidates as storage materials.

| Storage material | Gravimetric storage capacity (wt%) |
|---|---|
| LiH | 12.7 |
| $Mg_2NiH_4$ | 3.5 |
| $NaAlH_4$ | 3.7 |
| $MgH_2$ | 7.7 |
| $V(0.85)Ti(0.1)Fe(0.05) + H$ | 3.7 |
| $Li_2B_{12}H_{12}$ | 6.5 |
| $Na_3AlH_6$ | 1.9 |

**Table 2.** Gravimetric storage capacity of different materials used as hydrogen storage materials [10].

### 2.3. The improvement of hydrogen absorption by using ion implantation

Pure titanium is an element with a high affinity to hydrogen; however, it reacts with hydrogen at high temperatures, so in recent years some investigations have been carried out in order to improve the activation properties of this and other metals used as hydrogen storage materials. These methods include glow discharge in Al [11], ion mixing in TiFe [12], ion implantation in Ti [13], Pd [14], and $MgH_2$ [15].

The implantation process goes back to the nineteenth century and has been continually refined ever since. In the late 1940s and 1950s Robert Van de Graaff was the pioneer of accelerator construction, and the high-voltage technology, which was the base for building the first commercial ion implanters. One of the most common applications of ion implanters are the integrated circuit manufacturing, where doping or modifying silicon and other semiconductor wafers is the main goal.

Ion implantation is a process that involves generating an ion beam and impinging it into a substrate, so that the ions come to rest inside the material. During implantation, the ions

interact with nucleus and electrons of the substrate producing physical, electrical, and chemical changes in the material by transferring their energy and momentum to the electrons and atomic nuclei of the target material. When an energetic ion collides with a solid, it loses energy by two processes: (1) by inelastic or electronic process in which the electrons of the material are excited and (2) by elastic or nuclear collisions with the target atoms, producing structural changes, such as interstitials and vacancies. During the nuclear collisions, an ion can transfer enough energy to a matrix atom, becoming a projectile inside the material, and producing collision cascades. After losing its energy, when the ion or the released atom does not find any vacant space in the lattice, they tend to occupy any space in the solid known as interstitial. When the ions are implanted into a metal or metal alloy, the structural change is mostly produced in the surface of the material, creating pathways by which hydrogen can migrate into the metal in an easier way.

In this section, the results of a study of hydrogenation of pure titanium after ion implantation are presented.

The material used to carry out the study of hydrogen storage was pure titanium, manufactured by Goodfellow with 99.6% purity. The samples consisted of slices cut from titanium rods, which were polished, cleaned in acetone, and rinsed with deionized water. After the cleaning process, the materials were implanted at room temperature with a Colutron ion gun. The titanium samples were implanted with 5 keV H ions at a fluence of $1 \times 10^{14}$ ions/cm$^2$. With this process, we intentionally induced defect zones in the surface region that may accelerate the diffusion of hydrogen. After implantation, the samples were hydrogenated at 300, 450, and 600°C in a 50% hydrogen and 50% argon atmosphere, at 1 atm pressure, and a flux of 50 cc/min, during 2 h. We intentionally implanted hydrogen ions in order to avoid any element contamination in the material. The 5 keV energy was chosen in order to assure that the biggest damage and the highest number of vacancies produced during implantation, would be produced in surface.

**Figure 6** shows the hydrogen depth profile of the implanted and the nonimplanted samples hydrogenated at 450°C [13]. It can be observed in the figure that the hydrogen absorption of titanium without implantation is almost null, as can be verified in **Figure 4**; however, when a previous 5 keV H ions implantation is achieved to the metal, the scene is completely different and the hydrogen storage capacity of the metal is highly improved. Both curves in **Figure 6** show a small hydrogen peak at the surfaces of both titanium samples. These peaks are related to the superficial hydrogen in the nonimplanted sample (blue circles) and to the combination of the superficial hydrogen and the implanted hydrogen in the irradiated sample (red squares), where the hydrogen signal is slightly higher as a consequence of the implanted hydrogen. It can be also appreciated in **Figure 6** that the nonimplanted material does not absorb hydrogen beyond its surface. This can be confirmed in the ERDA graph as an almost null hydrogen signal beyond the 0.15 μm. In the case of the implanted materials, they show the same superficial hydrogen signal as the nonimplanted samples, but they also present a major hydrogen signal from 0.15 to 0.83 μm. In order to verify if the hydrogen continues beyond 0.83 μm into the bulk, ERDA measurements were performed from the back of the samples. The results showed that hydrogen is present through all the material.
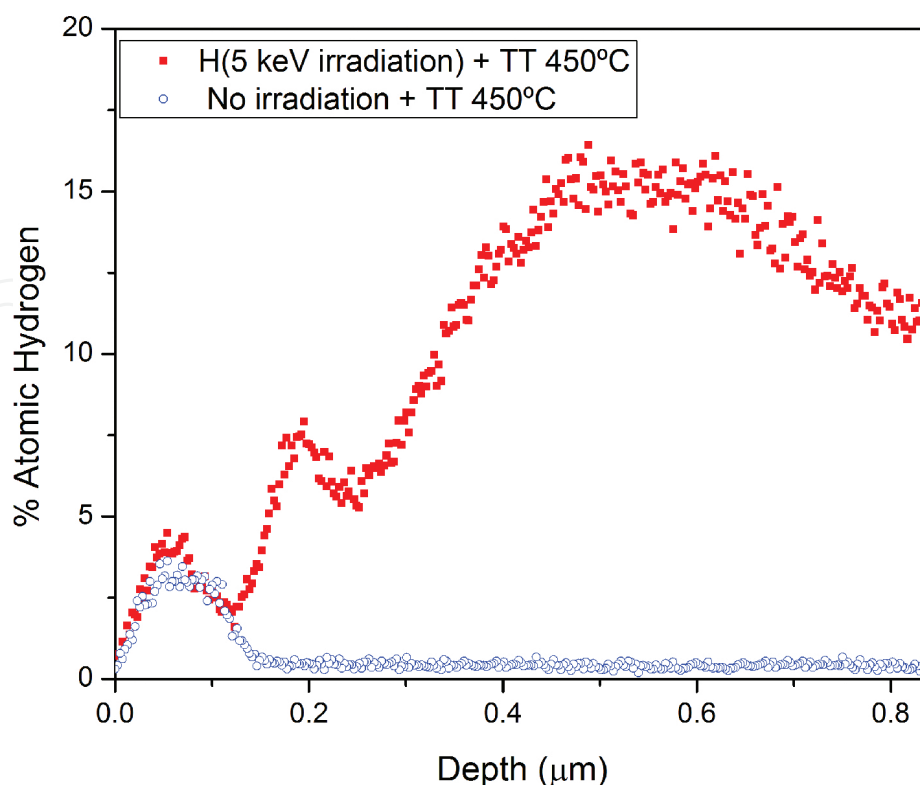
**Figure 6.** Hydrogen depth profile of pure titanium hydrogenated at 450°, with (red squares) and without (blue circles) implantation [13].

The high continuum hydrogen signal that can be observed in the implanted samples can be explained by means that during implantation strains in the surface region change, as well as structural changes are produced in the surface of the metal, introducing defects and dislocations and creating pathways in which hydrogen atoms can migrate into the metal. These paths may accelerate the diffusion of hydrogen through the metal, improving its storage capacities.

In **Figure 7**, a comparative between hydrogen concentration of the implanted [13] and the nonimplanted (see **Figure 4**) titanium samples after being hydrogenated at different temperatures is observed. These results were obtained directly by ERDA spectra using Eq. (1) and comparing with a reference sample of TiH$_2$. For 300°C, there is no difference between the hydrogen absorbed by the implanted and the nonimplanted samples; however, for temperatures above 450°C, the behavior is completely different, showing an improvement in the hydrogen content for the titanium samples previously implanted. In this way, when hydrogen ions are implanted into the pure titanium material, its activation temperature is reduced.

**Table 3** shows the gravimetric storage capacity of pure titanium samples after being implanted and hydrogenated [13]. The results show that as well as the hydrogen concentration, the storage capacity was improved after the 5 keV H ion implantation. When comparing with **Table 1**, it can be noticed that the storage capacity increased from 3.02 to 3.77% in the sample hydrogenated at 600°C during the activation cycle. This confirms that implantation process does accelerate the activation process of pure titanium. We can assure that cyclic hydrogena-

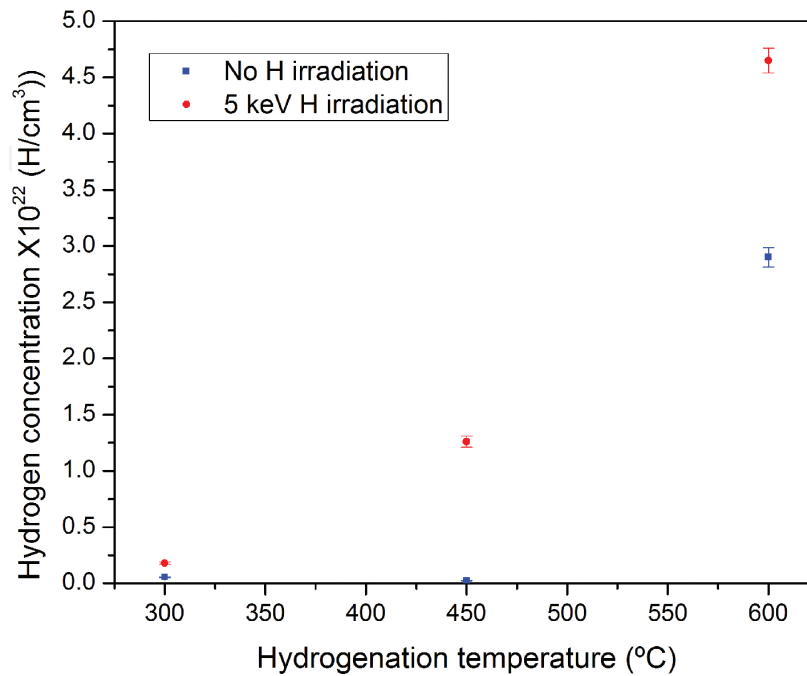tions must increase considerably the hydrogen absorption in pure titanium, as well as in the Ti-6Al-4V alloy.



**Figure 7.** Hydrogen concentration of the hydrogenated samples, before and after implantation [13].

| Hydrogenation temperature (°C) | Gravimetric storage capacity (wt%) |
|---|---|
| 300 | $0.097 \pm 0.007$ |
| 450 | $0.94 \pm 0.066$ |
| 600 | $3.77 \pm 0.264$ |

**Table 3.** Gravimetric storage capacity of titanium samples after implantation and hydrogenation [13].

In order to check if the hydrogen absorbed by the metal is forming hydrides, XRD analysis was conducted [13]. **Figure 8** shows the results of the XRD of the implanted and hydrogenated samples, as well as a pure titanium reference. The results show the diffractions of the titanium alpha phase. The titanium dihydride phase ($TiH_2$) is also observed, showing the (100) and (200) lines, which correspond to the higher diffractions. The results also show a decrease in the intensity in the pure titanium (101) reflection as the temperature of hydrogenation increases. This behavior could be the consequence of a structural change or loss of crystallinity produced during implantation, hydrogenation, or both. This figure also shows that the relative intensities of the reflections (100) and (002) in the HCP titanium were modified with the presence of hydrogen. This indicates that during hydrogen absorption a change in crystal orientation was induced. An important result obtained from this figure is that the implanted hydrogen does not produce hydrides in the metal, so the hydride phase is formed during hydrogenation.
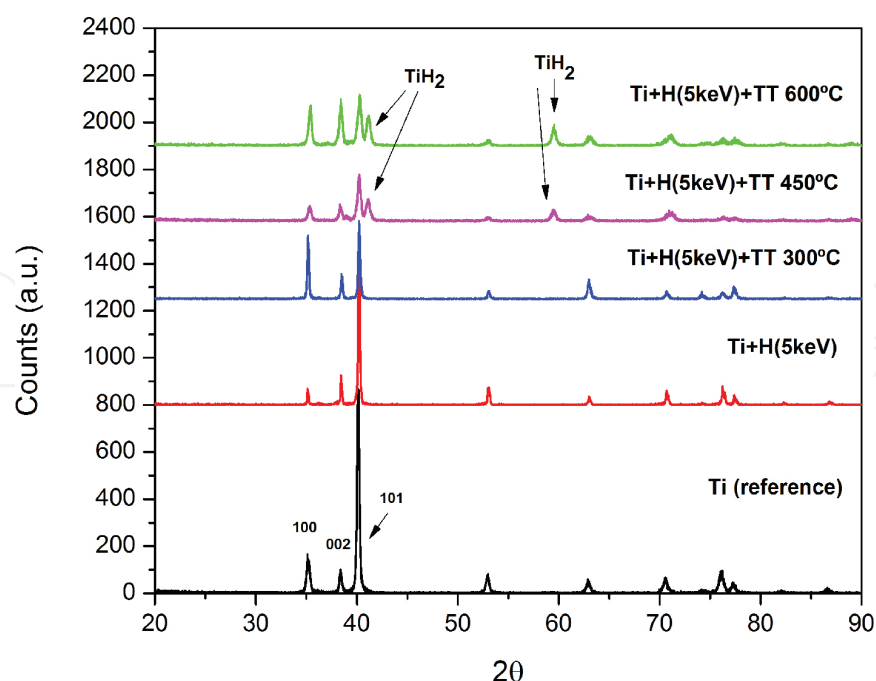
**Figure 8.** Comparative XRD patterns of five titanium samples: pure titanium (reference), titanium implanted with 5 keV H ions (Ti + H(5 keV)), and the three patterns in the top that correspond to samples implanted with 5 keV H ions and hydrogenated at different temperatures (Ti + H(5 keV) + TT) [13].

## 2.4. Hydrogen desorption of Ti and Ti-6Al-4V

If metal hydrides must considered as reliable fuel cells, it would be mandatory for them to become stable, which means that the materials must be enough stable for not releasing hydrogen when the metal is being stored. For this reason it is important to study the release of hydrogen under conditions of low temperature and atmospheric pressure. Studies were performed to determine the degree of release of hydrogen at atmospheric pressure and room temperature for samples of pure titanium and the Ti-6Al-4V alloy. Both materials were first hydrogenated using the same cleaning and hydrogenated experimental details as previously. After that, the samples were kept stored during 4 months; meanwhile their hydrogen desorption was measured using the ERDA technique.

The results showed in both materials that hydrogen was naturally released, which means that hydrogen is desorbed from materials, without providing any additional energy to the system. In the case of pure titanium, it was observed that hydrogen concentration decreases slower than the Ti-6Al-4V alloy does, showing a decrease of 30% of its total hydrogen concentration, after 130 days that remained stored. Furthermore, the alloy showed a greater decrease in hydrogen content, decreasing up to 40% after 130 days of storage. The decrements in hydrogen after both materials were stored for 1 day is almost null. These results suggest that these materials are good candidates for storing hydrogen, since they are quite stable. In terms of applications to the automotive industry, it means that the vehicle could remain stop during 4 months and it will only lose 30% of its fuel if a titanium cell were used.

### 2.5. The effects of hydrogen absorption and desorption in Ti and the Ti-6Al-4V alloy

As has been already mentioned, the absorption of hydrogen by metals, such as pure titanium and the Ti-6Al-4V alloy, can produce changes in their metallic structures, such as in its hardness.

Hardness measures the resistance of a material when a force is applied to it. In this way, hydrogen is an element that changes hardness when it is introduced into a metal. Hardness is defined as the ratio of the applied load $P$ to the indentation area $A$. In this way, Vickers microhardness ($H_v$) follows the relation

$$H_v = 1854 \frac{P}{d^2} \tag{4}$$

where $d$ is the diagonal of the indentation area.

Some works have been carried out in order to study the influence of hydrogen in hardness properties of pure titanium and the Ti-6Al-4V alloy [16]. Vickers microhardness tests were carried out on both materials at hydrogenation temperature ranging from 150 to 650°C. The results show that the mechanical properties of the metals were modified when hydrogen is absorbed into the material.

**Figure 9** shows the Vickers microhardness behavior of pure titanium versus hydrogenation temperature. As was mentioned before, hydrogen concentration is increased from 550 to 650°C and after that temperature hydrogen is kept constant. The same behavior is observed when microhardness measures were performed after the metal was activated, as is shown in **Figure 9** (red squares), where pure titanium shows a tendency to become harder as hydrogen increases. This fact is a direct consequence of the hydrogen that remains in interstitial sites inside the metal and was verified when hydrogen is desorb from the material. **Figure 9** also shows two other curves that correspond to the microhardness measures of the titanium after being stored for 4 months (green circles) and 10 months (blue triangles). As was mentioned below, hydrogen is lost with time after the samples had kept stored for several months. The larger hydrogen concentration that correspond to the sample that was hydrogenated at 650°C, show average decreases in the Vickers microhardness of 8 and 27% after being kept stored for 4 and 10 months, respectively. The samples that contained smaller hydrogen concentrations, such as the metals hydrogenated between 150 and 500°C, maintained their microhardness values almost constant with time. In the case of the Ti-6Al-4V alloy the scene is repeated, showing an average decrease in hardness of 7 and 20% after 4 and 10 months, respectively. In the same way, the samples with smaller hydrogen amounts did not show a significant loss of micro-hardness with time.

The XRD patterns of the hydrogenated samples also showed that the titanium hydride peaks did not present any change in form nor size when hydrogen was released in natural way. This observation can be understood as the loss of hydrogen concentration was only due to the interstitial hydrogen that is released while the samples are kept stored and it is not due to the

metal hydride that has formed inside the materials. This result shows that the interstitial hydrogen is the main contributor that increases and decreases hardness in pure titanium and the Ti-6Al-4V alloy. In this way, it is corroborated that hydrogen plays an important role in changing the mechanical properties of a material.
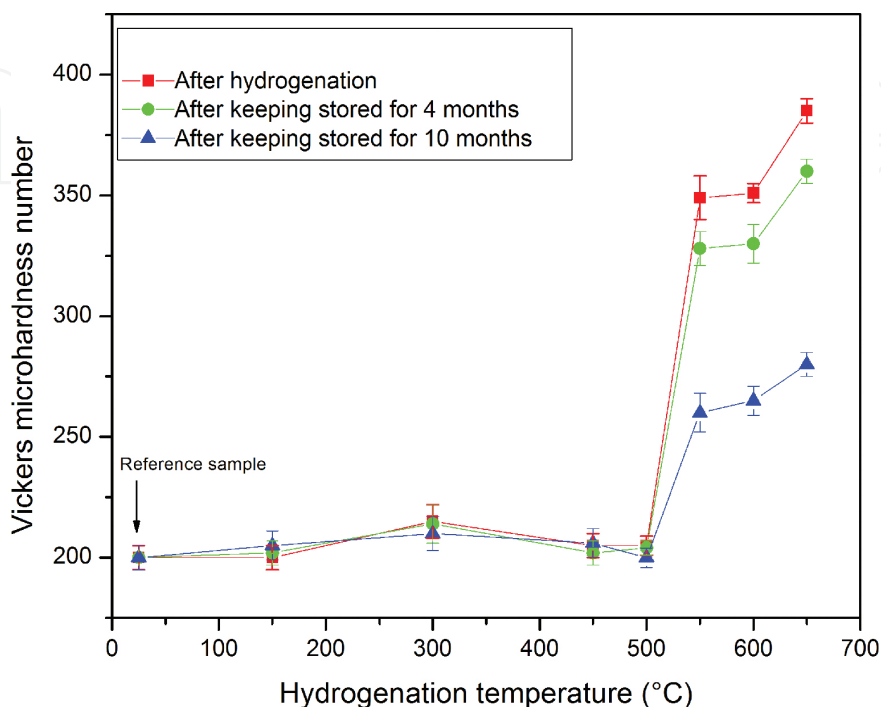


**Figure 9.** Vickers microhardness versus hydrogenation temperature for pure titanium samples. A reduction in hardness as the samples loose hydrogen with time can be observed [16].

## 3. Conclusions

The potential for storing hydrogen in metal hydrides is an area of material research that must be kept active. This chapter showed that pure titanium and the alloy Ti-6Al-4V are good candidates as hydrogen storage materials, which can increase their storage capacities after ion implantation. Ion implantation improves activation easing the diffusion of hydrogen through the whole material. It was also noted that the surface quality of the metal is important during hydrogenation in order to get better results during hydrogen absorption.

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## Author details

Alejandra López-Suárez

Address all correspondence to: chipi@fisica.unam.mx; chipi72@gmail.com

Physics Institute, National Autonomous University of Mexico, Mexico City, Mexico

## References

[1] Gray MacA E. Hydrogen storage status and prospects. Adv. Appl. Ceram. 2007; 106: 25–28. doi:10.1179/174367607X152380

[2] López-Suárez A, Rickards J, Trejo-Luna R. Analysis of hydrogen absorption by Ti and Ti-6Al-4V using the ERDA technique. Int. J. Hydrogen Energy. 2003; 28: 1107–1113. doi: 10.1016/S0360-3199(02)00202-1

[3] Yu XB, Yang ZX, Liu HK, Grant DM, Walker GS. The effect of a Ti-V based BCC alloy as a catalyst on the hydrogen storage properties of $MgH_2$. Int. J. Hydrogen Energy. 2010; 35: 6338–6344. doi:10.1016/j.ijhydene.2010.03.089

[4] Alefeld G, Völkl J, editors. Hydrogen in Metals I. 1st ed. Germany: Springer Verlag; 1978. 428 p. doi:10.1007/3-540-08705-2

[5] Blackburn JL, et al. Measurement of the reversible hydrogen storage capacity of milligram Ti-6Al-4V alloy samples with temperature programmed desorption and volumetric techniques. J. Alloys Compd. 2008; 454: 483–90. doi:10.1016/j.jallcom. 2007.01.006

[6] Chu WK, Mayer JW, Nicolet MA. Backscattering Spectrometry. 4th ed. New York, USA: Academic Press; 1978. 384 p. doi:10.13140/RG.2.1.1948.0807

[7] Tesmer JR, Nastasi M, editors. Handbook of Modern Ion Beam Materials Analysis. 2nd ed. Pennsylvania, USA: MRS; 2010. 370 p. ISBN 9781605112176.

[8] López-Suárez A. Influence of surface roughness on consecutively hydrogen absorption cycles in Ti-6Al-4V alloy. Int. J. Hydrogen Energy. 2010; 35: 10404–10411. doi:10.1016/j.ijhydene.2010.07.163

[9] Lee SM, Perng TP. Effect of the second phase on the initiation of hydrogenation of $TieFe_{1-x}M_x$ (M = Cr, Mn) alloys. Int. J. Hydrogen Energy. 1994; 19: 259–263. doi: 10.1016/0360-3199(94)90095-7

[10] Yang J, Sudik A, Wolverton C, Siegelw DJ. High capacity hydrogen storage materials: attributes for automotive applications and techniques for materials discovery. Chem. Soc. Rev. 2010; 39: 656–675. doi:10.1039/b802882f

[11]  Saitoh H, Hjima Y, Tanaka H. Hydrogen diffusivity in aluminium measured by a glow discharge permeation method. Acta Metall. Mater. 1994; 42: 2493–2498. doi: 10.1016/0956-7151(94)90329-8

[12]  Suda T, Ohkawa M, Sawada S, Watanabe S, Ohnuki S, Nagata S. Effect of surface modification by ion implantation of hydrogenation properties of TiFe alloy. Mat. Trans. 2002; 43: 2703–2705. doi:10.2320/matertrans.43.2703

[13]  López-Suárez A, Valencia CE, López-Patiño J, Vargas MC, Fuentes BE. Improvement of titanium hydrogenation by low energy ion irradiation. Int. J. Hydrogen Energy. 2015; 40: 4194–4199. doi:10.1016/j.ijhydene.2015.01.166

[14]  Abe H, Uchida H, Azuma Y, Uedono A, Chen ZQ, Itoh H. Improvement of hydrogen absorption rate of Pd by ion irradiation. NIMB. 2003; 206: 224–227. doi:10.1016/S0168-583X(03)00734-1

[15]  Grbovic-Novakovic J, Matovic LJ, Drvendzija M, Novakovic N, Rajnovic D, Siljegovic M, Kacarevic-Popovic Z, Milovanovic S, Ivanovic N. Changes of hydrogen storage properties of $MgH_2$ induced by heavy ion irradiation. Int. J. Hydrogen Energy. 2008; 33: 1876–1879. doi:10.1016/j.ijhydene.2008.02.008

[16]  López-Suárez A, Rickards J, Trejo-Luna R. Mechanical and microstructural changes of Ti and Ti–6Al–4V alloy induced by the absorption and desorption of hydrogen. J. Alloys Compd. 2008; 457: 216–220. doi:10.1016/j.jallcom.2007.03.031