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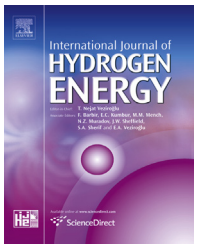

Improvement of titanium hydrogenation by low energy ion irradiation

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ABSTRACT

In this work a study of the improvement of titanium hydrogenation by low energy ion irradiation is presented. 3 mm titanium slices were irradiated at room temperature with 5 keV H ions and annealed at different temperatures (300, 450 and 600 °C) in a hydrogen atmosphere in order to study the absorption of hydrogen. ERDA measurements as well as X-ray diffraction analysis show an improvement in hydrogen absorption relative to those samples that were not irradiated previously to hydrogenation.

Introduction

Pollution and environmental problems associated to transportation and usage of fossil fuels are the driving forces behind research into alternative and green energies. Hydrogen is the ideal energy source to replace hydrocarbons and it can be used in a fuel cell to generate clean energy, due to water is the only sub-product when burning. Production of hydrogen is also a straight-forward process from a wide range of sources, including solar, wind, geothermal and hydroelectric power [1].

In terms of hydrogen storage, metal hydrides have been the best option to store hydrogen because they can absorb large amounts of hydrogen at a constant pressure. Many transition metals and their intermetallic alloys have been used as hydrogen storage media due to their capacity to react with hydrogen and to form hydrides. The metal hydride formation takes places through hydrogen molecules that interact with the atoms of the surface of a material through dispersive forces known as physisorption or physical adsorption. In this way, molecular hydrogen is dissociated and adsorbed at the surface of the metal with the subsequent hydrogen ions diffusion into the bulk of the material; when energy increases, the hydrogen atoms occupy the available interstitial sites in

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the metal lattice. Upon all these interstitial sites are occupied, the metal is not able to absorb more hydrogen atoms, so in order to avoid this inconvenience; the metal becomes a metal hydride, where two phases can coexist: metal and metal hydride. The great advantage of metal hydrides over other hydrogen storage media, such as activated carbon, carbon nanotubes or zeolites is that the released hydrogen of the metal hydrides is extremely pure, which is an important factor when considering hydrogen for mobile applications [2-4].

Pure titanium is an element with a high affinity to hydrogen; however it reacts with hydrogen at high temperatures [5]. In order to avoid this problem, intermetallic compounds, such as $TiMn_2$, TiFe and Ti_2Ni, have been used as hydrogen storage materials because their capacity to absorb hydrogen at much lower temperatures than pure titanium.

Investigations have been carried out in order to improve the activation properties of several metals. Some of these methods include ion implantation and ion mixing in TiFe [6] and glow discharge in Al [7]. In both cases, an enhancement in the initial activation energy was reported. In order to improve hydrogen absorption in pure titanium, a study of low energy ion implantation into the metal is presented in this work. Ion implantation is a process by which ions of a certain material are accelerated and impacted into a solid. During implantation, the ions interact with electrons and nucleus of the target 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. The ion interaction causes structural changes, such as vacancies and interstitials. Vacancies are crystal lattice points unoccupied by an atom formed when the ion collides with a target atom, resulting in transfer of a significant amount of energy to the target atom such that it leaves its crystal site. If enough energy is transferred to the atom, it becomes a projectile in the solid, and can cause successive collision events. Interstitials result when the ion or the released atom lose their energy and come to rest in the solid, but find no vacant space in the lattice to reside. When the energy of the implanted ion is low, the structural change caused is produced in the surface of the material, creating pathways by which hydrogen can migrate into the metal in an easier way.

Once hydrogen is absorbed into the medium, it's accurately measurement is quite important. The most common ways of measuring hydrogen absorption are: the Sieverts-type volumetric method, which measures the change in hydrogen pressure when hydrogen is absorbed; the gravimetric method, which directly measures the hydrogen absorbed by the sample; and the flow controlled volumetric method, which measures the amount of gas by integrating the gas flow over the period of time required to fill the sample [8,9].

Although these hydrogen sorption measurements apparatus are very common, they present some inconvenience. For instance, the Sieverts technique shows a poor reproducibility and discrepancies in measurements for a given sample [10,11]. In the gravimetric technique, the gas to the system can create temperatures gradients and convention currents that can result in signals as large as the values to be measured. In the flow controlled volumetric method, there is not control over the hydrogen that is adsorbed on the chamber surface [12,13].

In order to avoid these problems, ERDA (Elastic Recoil Detection Analysis) technique is one of the best options to measure the amount of hydrogen stored by the sample immediately after the absorption process takes place. ERDA technique was originally developed for hydrogen detection and the main advantages are its ability to obtain quantitative depth profiling information of the elements contained in the sample in one measurement, as well as its great accuracy and excellent depth resolution [14]. The combination of the depth resolution less than 1 nm and its detection limit of 0.1 atomic %, give ERDA technique significant advantages over other surface analysis methods for measuring hydrogen. In the ERDA technique 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 foil used to stop particles heavier than hydrogen, before reaching 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 ERDA spectra. 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 [14].

In this work a study of the improvement of titanium hydrogenation by low energy ion irradiation is presented. 3 mm titanium slices were irradiated with 5 keV H ions and annealed at different temperatures in a hydrogen atmosphere in order to absorb hydrogen. The results show an improvement in hydrogen absorption relative to those samples that were not irradiated previously to the hydrogenation.

Experimental procedure

Titanium samples manufactured by Goodfellow with 99.6% purity were used as the storage material. The samples consisted of 3 mm thick slices cut from 9.5 mm diameter titanium rods which were annealed in argon at 675 °C by the manufacturer. After cutting, they were polished using Emery paper and then were ultrasonically cleaned in acetone, followed by rinsing with deionized water in order to remove any kind of impurity from the surface of the sample. Afterwards, the samples were implanted at room temperature with 5 keV H ions at a fluence of 1×10^{14} ions/cm^2, using a Colutron ion gun at the Facultad de Ciencias, UNAM. After implantation, the samples were hydrogenated at 300, 450 and 650 °C in a 50% hydrogen and 50% argon atmosphere, at 1 atm pressure, and a flux of 50 cc/min, during 2 h. In addition, in order to estimate the H ion ranges, Monte Carlo SRIM calculations were performed.

Hydrogen depth profile distributions were determined by ERDA at the Instituto de Física 3 MV 9SDH-2 Pelletron accelerator. The samples were irradiated with a collimated 3 MeV α-particle of 1 mm diameter, the incident current was 50 nA and the integrated beam charge was 30 μC. The surfaces of the samples were placed at an angle of 15° with respect to the incoming beam; meanwhile, a surface barrier detector, used to detect the hydrogen recoils, was placed at an angle of 30° to the beam direction. A 12 μm thick Mylar foil was used in front of the detector to stop elastically scattered ions heavier than recoil hydrogen. A film of Kapton polymer ($C_{22}H_{10}N_2O_5$) was