Hydrogen storage in metal hydrides, synthesis and characterization

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Abstract. One of the keys to the implementation of the hydrogen economy is its safe and efficient storage. One of the most promising methods is metal hydrides. In this work, the influence of the mechanical grinding process on the properties of the TiCr₁₁V₀₉ alloy, specifically the absorption and desorption capacities, and structure of the hydride was studied. The maximum storage capacity was 3.2% wt. at a temperature of 40°C and pressure of 10 bars, observing two types of hydrides TiCr₁₈H₅₃ with a body centred cubic (BCC) structure and TiH₂ with face centred cubic (FCC) structure, which release hydrogen in two temperature ranges.

1. Introduction
The sustainable development of the countries implies the need for a system of energy supply that is safe, accessible and economical, therefore many countries have focused their efforts on implementing renewable energies, since they respond to most of these requirements [1].

In this context, the hydrogen economy emerges as a viable alternative to produce energy and use it in mobile applications. Hydrogen is considered as a vector of clean energy and high energy density, which makes it one of the best options for both mobile and stationary applications. However, one of the keys to the implementation of the hydrogen economy is its safe and efficient storage [2]. The metal hydrides are characterized by having high hydrogen storage capacity, for example MgH₂ has a capacity of 7.6% wt and Ti-Cr-V alloy has a capacity of 3.9% wt. [3-6].

In this sense, the investigations are focused on providing a solution to the problems related to how to increase the storage capacity of hydrogen in a safe, efficient and technologically applicable way to be used by most of the world population.

The objective of this investigation was to study the influence of the mechanical grinding process on the properties of the TiCr₁₁V₀₉, specifically the absorption and desorption capacities, and structure of the hydride.

2. Materials and method
The elements to form the alloy had a purity greater than 99.999% and were melted in an arc furnace under an argon atmosphere. An ingot of 30g was taken, which was melted 4 times to ensure good homogeneity. Subsequently, it was divided into three samples, each one of 10g. The first one was pulverized by a mortar and the second and third were milled using a planetary mill at 300rpm for 1 and 3 hours respectively under a hydrogen atmosphere.
The samples were activated to remove from the surface the moisture and metal oxide residues and were hydrogenated in an autoclave at pressure of 10bar and temperature of 40°C. The characterization was carried out through of X-ray diffraction (DRX), temperature programmed desorption (TPD) and differential scanning calorimetry (DSC).

3. Results and discussion
Initially the samples were hydrogenated, the absorption capacity was observed by the technique temperature-programmed desorption (TPD), this method is used to investigate the events that take place at the surface of solid material while its temperature is changed in a controlled manner [7]. The absorption capacity given by the TPD technique is shown in the Table 1.

| Alloy         | Treatment method                                    | Absorption capacity (%wt.) |
|--------------|-----------------------------------------------------|----------------------------|
| TiCr$_{1.1}$V$_{0.9}$ | Mortar                                             | 3.4                        |
| TiCr$_{1.1}$V$_{0.9}$ | Planetary mill at 300 rpm for 1 hour               | 0.4                        |
|              | Planetary mill at 300 rpm for 3 hours               | 0.8                        |

Table 1. Hydrogen absorption capacity by TPD.

Figure 1 shows the X-ray diffraction pattern obtained by TPD of the first sample studied which was pulverized by mortar. The alloy TiCr$_{1.1}$V$_{0.9}$ presents a BCC structure, which is modified when hydrogen is absorbed in the crystalline network, similar results were obtained by [8]. Are possible observed two types of hydrides, the first one is TiCr$_{1.8}$H$_{5.3}$ with a structure FCC and the second is TiH$_2$ with a BCC structure.

Figure 2 and Figure 3 show the diffraction patterns of the samples milled by planetary mill for 1 hour and 3 hours respectively. Only the formation of second hydride TiH$_2$ is observed, which is formed in the first stage of hydrogen absorption where the operating pressure is high, as observed by [9]. The first TiCr$_{1.8}$H$_{5.3}$ hydride is not formed, due to the contamination of the samples by the interaction with the steel spheres of the planetary mill. This contamination leads to decrease in absorption capacity, as observed by [10-11]. This is corroborated with the absorption data given by the TPD technique and shown in Table 1.
Figure 2. DRX of second sample milled by planetary mill for 1 hour.

Figure 3. DRX of third sample milled by planetary mill for 3 hours.

Figure 4 shows the thermograms obtained by DSC. The endothermic peaks for the different hydrogenated samples were observed. The first alloy, who was pulverized by mortar, it presents two characteristic peaks of the hydrides formed. The first was TiCr_{1.8}H_{5.3} that releases a greater amount of hydrogen in a temperature range between 217 and 312°C, this sample unlike those milled presents less contamination, therefore, the diffusion and desorption of hydrogen is facilitated; this is evidenced by the work carried out by Martinez et al [12]. Furthermore, is observed on the sample milled for three hours an exothermal peak in 100°C due to release of water, the sample had humidity because they were treated at room temperature, however it does not affect the performance of the alloys.

The BCC phase of TiH_{2} initiates the desorption at a higher temperature in the three samples between 390-580°C; however, for samples milled for 1 and 3 hours only the desorption of TiH_{2} was observed, this is due to in these samples the first hydride did not form.
Figure 4. DSC of the samples TiCr$_{1.1}$V$_{0.9}$.

4. Conclusions
A high storage capacity for the TiCr$_{1.1}$V$_{0.9}$ alloy was showed. The high amount of vanadium allows lower desorption temperatures because it inhibits the formation of undesirable laves phases. This type of alloys is very susceptible to contamination as observed in the samples milled for 1 and 3 hours, this contamination is mainly due to the spheres used in the process were made of steel, therefore an optimal activation process is important.

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