Influence of mechanical milling on the hydrogen absorption properties of TiCrV – based alloys

A Martinez-Amariz¹, and D Peña Ballesteros²
¹ Grupo de Investigación en Nuevas Tecnologías, Universidad de Santander, Bucaramanga, Colombia
² Grupo de Investigación en Corrosión, Universidad Industrial de Santander, Bucaramanga, Colombia

E-mail: alejandrom@udes.edu.co

Abstract. The hydrogen economy is a concept focused on this element as a carrier of clean and cheap energy, one of the keys is the storage of this gas safely. In this sense, TiCrV-based alloys have great capacity to store hydrogen. In the present working studied the influence of the process of mechanical milling of high energy in the storage capacity of hydrogen of TiCr1.1V0.9 alloy. The alloy was synthesized by arc fusion and manually crushed. The effects of mechanical milling were studied for periods of time of 1 hour and 3 hours at 300 revolutions per minute with a weight/weight ratio of the sample 10: 1. The x-ray diffraction analyzes revealed solid phase formation of body center cubic phase, characteristic of TiCrV base alloys, and formation of TiCr1.8H5.3 hydrides and TiH2 hydrides with orthorhombic structure and body center cubic, respectively. The hydrogen storage capacity of the TiCr1.1V0.9 alloy decreased with the increase in grinding time. The reasons for the drop in hydrogen storage capacity are mainly two: contamination of the surface of the alloy powder and changes in the microstructure generated by the plastic deformation in the grinding process. However, an increase in absorption kinetics was observed at longer milling times because the surface area increases since the crystallite size decreases. This phenomenon can be explained by the catalytic effect produced by the decrease in the particle size of the samples. The differential scanning calorimetry analysis was able to determine that the TiCr1.8H5.3 hydrde stored a greater amount of hydrogen and has a lower desorption temperature compared to the TiH2 hydrde.

1. Introduction

Currently, a high percentage of the world’s energy demand is covered by fossil fuels such as natural gas, oil and coal. The world energy demand is approximately 13 terawatts per year, which is supplied in 87% by fossil fuels and it is estimated that by 2050 it will take around 30 terawatts per year to supply the world population’s energy demand [1] However, fossil fuels are non-renewable energy resources and it is estimated that in the coming decades there will be a significant decrease in their availability and production. On the other hand, the combustion of fuels of fossil origin gives rise to the emission of CO2, which is the main responsible for global warming and climatic changes related to our planet.

Therefore, serious global and regional policies are necessary to mitigate the current problems and it is the development of new environmentally friendly energies, the solution. One of the answers to the energy crisis that is coming is the use of hydrogen as an energy source and its transformation into electricity through the so-called fuel cells or cells. A fuel cell is an electrochemical device where hydrogen combines with oxygen to directly produce electricity [2].
Hydrogen is considered a promising candidate as an energy vector because it exhibits the highest energy content per unit of weight compared to any fuel. As a fuel, hydrogen stands out due to its high oxidation reaction, which releases an energy of 242 KJ/mol, which is three times higher than the calorific value obtained from the combustion of hydrocarbons and other fossil fuels, and hydrogen is friendly to the environment due to its clean combustion [3].

Thus, the term "hydrogen economy" responds to a vision of the future where this gas generated cleanly and economically would serve to feed the bulk of the energy needs of society. This proposal will mitigate the existing dependence of human civilization on fossil fuels, since hydrogen could be produced directly from the dissociation of water, for example, using energy sources such as renewable or nuclear. Likewise, the emission of greenhouse gases and, consequently, atmospheric pollution, would be significantly reduced, since the combustion of hydrogen in a fuel cell is water [4]. These cells offer a promising approach to a future with clean, abundant and economic energy.

In the last two decades, multiple investigations are being carried out to develop new methods and systems for the storage of hydrogen. Research has shown that chemical or physical storage of hydrogen in transition metal-based materials due to the formation of metal hydrides has potential advantages compared to current storage methods [5-6]. A. Züttel, et al. [3] reports that the complex hydride of LiBH4 reaches a hydrogen absorption capacity of 13.5% by weight. J.A. Puszkiel, et al. [7] points out that the magnesium hydride MgH2 family has a hydrogen absorption capacity of 7.6% by weight, in addition to a high energy density (9 MJ/kg of Mg), which points to magnesium hydrides as one of the most attractive materials for the storage of hydrogen. On the other hand, Martinez et al [8] mention that the hydrides of intermetallic compounds of TiCrV base alloys reach a hydrogen absorption of 3.6% by weight, with absorption and desorption temperatures of 30 °C and absorption pressures of 17 bar and desorption of 0.5 bar, besides having attractive advantages such as rapid kinetic absorption-desorption and stability at room temperature. For this reason, metal hydrides are seen as a promising alternative for the storage of hydrogen in the solid state [9-10].

In this context, the hydrogen storage in solid compounds through physicochemical reactions appears as a very promising alternative given its versatility, many of the hydrides mentioned are capable of storing more hydrogen per unit volume than liquid hydrogen itself [11], presenting greater safety. The suitability of solid compounds to absorb and desorb hydrogen depends on parameters such as pressure and charge/discharge temperature, the kinetics of these processes, as well as their cyclability. These properties are closely linked to the thermodynamic and kinetic properties of formation and decomposition of hydrides. Therefore, characterizing the Gibbs energy of the reaction, as well as the activation energies of the different stages that occur during the absorption/desorption of hydrogen in the material, is vital to study its potential application [12].

From an application point of view, storing energy through metal hydrides opens up a great possibility of implementing large-scale renewable energies in Colombia, since the excess of these can be accumulated and used at times where renewable energy has fewer efficiency spikes.

The influence of the high-energy mechanical grinding process on the hydrogen storage capacity of the TiCr1.1V0.9 alloy was studied in this research paper. The alloy was produced by arc fusion and manually crushed. The effects of mechanical milling were studied for periods of time of 1 hour and 3 hours at 300 revolutions per minute (RPM).

2. Experiment methodology
The alloys were formed using arc melting in gettered Argon using high-purity materials (> 99.95). For this purpose, 20 g ingots respectively made of TiCr1.1V0.9, were used and the samples were smelted 3 times in order to achieve a homogenized microstructure.

The alloy of TiCr1.1V0.9 obtained in the form of ingot was crushed in a mortar with a controlled atmosphere of argon. Then, the load was divided into 3 samples of the same weight each and deposited in previously labeled containers.

The three samples of TiCr1.1V0.9 were prepared inside a glove box with controlled argon atmosphere for subsequent mechanical grinding. The first sample for milling was poured into a tungsten carbide...
container and the stainless steel balls were added, then the container was sealed tightly inside the same glove box and proceeded to transfer the sample to the mill. In this same way the other samples were prepared.

Subsequently, the first sample was placed in the sample holder inside the mill, the mill was secured and activated by selecting the corresponding variables in the planetary mill program. The same procedure was repeated for the other samples. Table 1. shows the variables of the mechanical grinding process for each sample. Sample No.1 was obtained by the manual crushing process, while samples No. 2 and 3 after the crushing process were obtained by mechanical grinding for 1 hour and 3 hours respectively.

| No of Alloy | Grinding speed (rpm) | Weight ratio balls/weight sample | Grinding Time (h) |
|------------|----------------------|----------------------------------|------------------|
| 1          | 300                  | 10:1                             | 0                |
| 2          | 300                  | 10:1                             | 1                |
| 3          | 300                  | 10:1                             | 3                |

For structural study was necessary to use the sample metal powder which passed through a mesh of 270 microns, following which it was subjected to X-Ray diffraction (XRD) using a Shimadzu 5000 with Cu-Kα radiation.

The hydrogen absorption properties of the as-cast sample were measured in a Sievert’s type apparatus (PCT pro 2000). The activation of the samples was carried out in an autoclave where a vacuum was maintained for 2 hours at 350 °C, the main objective being to remove any oxide layer and surface water ensuring the initial activation of the sample.

3. Analysis and discussion of results

3.1. Scanning electron microscopy analysis

In Figure 1. the TiCr1.1V0.9 alloy sample obtained by manual crushing using a special steel mortar is presented, here an average size of the order of 50 micrometres is observed, accompanied by an analysis by energy dispersive spectroscopy (EDS) where the characteristic peaks of the elements Ti, Cr, V are observed. In Figure 2. the alloy obtained by mechanical milling by 1 hour is presented, it is shown that the process decreases the size of the particles allowing an increase in the surface area; EDS shows the characteristic peaks of Ti, Cr, V and a small peak of Fe that is caused by the contamination of steel spheres. Finally, in Figure 3. the alloy obtained by mechanical milling by 3 hours is presented, with a decrease in particle size while maintaining the Fe peak.

Figure 1. (a) SEM micrograph of the manually crushed TiCr1.1V0.9 sample and (b) EDS analysis.
The analysis of surface morphologies by scanning electron microscopy (SEM) revealed that, after mechanical milling, the material presented smaller particles and is composed of particle agglomerates deformed, compared to the manually shredded sample. The particle size of the samples was analyzed by software, for this measurement about 50 particles were taken and the average was calculated. Table 2. shows the results, where a decrease in particle size is observed at a longer grinding time.

| Samples                        | Particle size (µm) |
|--------------------------------|--------------------|
| Manually crushed               | 94.6               |
| Mechanical grinding by 1 hour   | 57.3               |
| Mechanical grinding by 3 hour   | 39.7               |

3.2. Absorption properties

Figure 4. shows the hydrogen absorption curves for TiCr$_{1.1}$V$_{0.9}$ samples. The samples were previously activated in vacuum without the presence of hydrogen to break the barrier formed by the passive layer created on the surfaces of the samples.

The Figure 4(a). shows the hydrogen absorption kinetics in the manually crushed sample, a long incubation time of about 35 minutes is observed during the process of hydrogen absorption. This incubation time may be due to the presence of oxide layers and impurities present on the surface, which
could not be removed during the activation process. The surface impurities act as a barrier in the process of hydrogen diffusion and therefore hinder the penetration of hydrogen into the interior of the alloy structure. This behavior is characteristic of the TiCrV base alloys which need exposure to high hydrogen pressures for the dissolution of the passive layer and in this way, mitigate long incubation times [13-14].

![Figure 4](image)

**Figure 4.** Hydrogen absorption curves for TiCr$_{1.1}$V$_{0.9}$ alloy samples obtained by (a) manual crushing, (b) mechanical grinding for 1 hour and (c) mechanical grinding for 3 hours.

In the Figure 4(b), can be seen that after 1 h of grinding the alloy decreases the incubation time to 16 minutes, nevertheless the hydrogen absorption capacity decrease to 2.5% by weight. On the other hand, the Figure 4(c). shows the absorption curve of the mechanically ground sample for 3h, here the incubation time decrease to 5 minutes, reaching an absorption capacity of 1.6% by weight of hydrogen. This behavior suggests that the increase in grinding times increases the absorption kinetics of the TiCr$_{1.1}$V$_{0.9}$ alloy.

The increase in absorption kinetics can be explained in terms of the average particle size of the alloy which acts positively, decreasing both the incubation time and the time of absorption of hydrogen in the alloy studied. The decrease of the incubation time is due to the increase of the surface area generated by the reduction of the particle size, since the hydrogen atoms can be distributed more easily and in greater quantity on the surface, quickly breaking the barrier produced by the layer of oxide and impurities. Once the clean surfaces are created, the hydrogen atoms diffuse faster in the crystal lattice, locating in the interstitial sites saturating the solid hydrogen solution alloy, until reaching the maximum absorption capacity in the alloy.

However, a loss in the hydrogen absorption capacity of the samples obtained by mechanical grinding is observed compared to the sample that was not obtained by this mechanism. During the mechanical grinding process, the alloy particles are constantly trapped between the stainless-steel balls, generating wear of the balls and therefore Fe contamination in the alloy. On the other hand, the continuous shock between the particles and the balls generates plastic deformation of the particles.

This characteristic is produced by the generation of a large number of dislocations, as well as by other defects in the crystal lattice [15]. Therefore, in the diffusion process the hydrogen atoms find barriers to be located in the interstitial sites of the unit cell, in addition to the volumetric contraction of the cell generated by the contamination by Fe. This indicates that the contamination by Fe could be the main control factor in hydrogen storage capacity.
Mechanical grinding is a promising processing route to produce powder materials for the storage of hydrogen in TiCrV base alloys. However, the storage capacity of hydrogen in the structure was influenced by Fe contamination. Therefore, to avoid contamination of the alloy, an optimization of the processing parameters is needed.

4. Conclusions
The study of the mechanical grinding process in the hydrogen storage capacity of the TiCr$_{1.1}V_{0.9}$ alloy showed that the increase in grinding times induced a decrease in the hydrogen absorption capacity due to the excessive contamination by Fe in the samples, since the addition of Fe in the crystal lattice caused the contraction of the crystal lattice volume.

The hydride of TiCr$_{1.8}$H$_{5.3}$ could be used in some practical application since it desorbs the hydrogen stored in its structure at moderate temperatures, in addition its formation occurs at low pressures in comparison to the hydride of TiH$_2$ which has greater thermal stability and is formed at high pressures.

Mechanical grinding is a promising processing route to produce powder materials for the storage of hydrogen in TiCrV base alloys, since at longer grinding times the kinetics of hydrogen absorption in the samples studied improved markedly. However, it is necessary to optimize the processing parameters to mitigate the contamination by Fe in the materials.

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