A structural study of the hydrogen absorption properties by replacing vanadium with zirconium in metal alloys

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Abstract. Hydrogen storage and microstructure the TiCrV₀.₉, TiCrV₀.₉Zr₀.₂ and TiCrV₀.₇Zr₀.₄ alloys were investigated. The alloys were melted in arc furnace, the structure was analysed by X-ray diffraction and hydrogen absorption times were analysed by Sievert’s type apparatus. The results showed that the addition of Zr replacing the V decreases in the absorption capacity passing of 3.8%wt to 2.0%wt in contrast the speed of hydrogen absorption increases considerably.

1. Introduction
Eighty-seven percent (87%) of global energy demand is covered by fossil fuels such as carbon, petroleum and gas. From an environmental point of view, the use of fossil fuels is the main culprit in global warming, as well as causing serious respiratory problems in major cities due to pollution [1].

This state of affairs is unsustainable over the medium-term and as such it is necessary to find different forms of energy production and consumption that are clean, safe and dependable. One possible response to this crisis is to implement the use of hydrogen as a fuel source. This falls within a framework known as the “hydrogen economy”, a term currently used to refer to an alternative economic model not based on using fossil fuels for powering transportation.

Using hydrogen as an energy vector could revolutionize our immediate future [2]. The main advantage of hydrogen is that it is the most abundant element on Earth: it is present in water as well as fossil fuels; it is found in the Universe; and its combustion does not result in harmful emissions such as carbon dioxide which results from burning petroleum. The main challenge, however, is that hydrogen is rarely found in pure form making it difficult to exploit it effectively.

In this sense, the storage process for hydrogen is key. Traditional storage methods are conceptually simple using pressurized tanks or cylinders, or liquid hydrogen. Currently, researchers are investigating the use of metallic hydrides to store it in solid form.

One safe storage method for hydrogen in solid state is to use what are called H₂ storage alloys that result from forming metallic hydrides. The main advantages that make metallic hydrides very attractive, and are worth mentioning, include the high volumetric storage density, stability, safety and ease of handling. [3]

Ti-based hydrides have long been studied due to their relatively high hydrogen absorption capacities at room temperature, such as TiCrV which can store between 3.5 and 3.7% in weight, and presents optimum stability and cyclability properties meaning that it can be reused many times over [4].

In this work I seek to structurally characterize and study the hydrogen absorption TiCrV based alloys by adding Zr to replace V.
2. Experiment methodology
The alloys were formed using arc melting in atmosphere of argon using high-purity materials (>99.95). For this purpose, 20g ingots respectively made of TiCr_{1.1}V_{0.9}, TiCr_{1.1}V_{0.9}Zr_{0.2}, TiCr_{1.1}V_{0.7}Zr_{0.4}, were used and the samples were smelted 3 times in order to achieve a homogenized microstructure.

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 XRD (X-Ray Diffraction) using a Shimadzu 5000 with Cu-K\(\alpha\) radiation and the lattice parameters were calculated.

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
During the first stage of the process, an alloy was cast based on it is high hydrogen absorption capacities, with the stoichiometry TiCr_{1.1}V_{0.9}. Two other alloys were cast: TiCr_{1.1}V_{0.9}Zr_{0.2} y TiCr_{1.1}V_{0.7}Zr_{0.4}. One of the objectives is to diminish the amount of V and increase the Zr content since the use of V in technological applications is very expensive, and Zr also has a high affinity for producing hydrides.

3.1. XDR analysis
In Figure 1(a) it can be observed that the diffractogram corresponds with a body-centred cubic structure (bcc) characteristic of this kind of alloy, giving results that correspond with those reported by [4].

This body-centred cubic structure can be expected given that V and Cr have a bcc, and Ti crystalized into this same structure at temperatures above 800°C. As such only a single-phase was expected.

These kinds of compounds based on solid solutions with bcc structures demonstrate high hydrogen absorption rates at room temperature.

![Diffractogram](a) ![Diffractogram](b) ![Diffractogram](c)

Figure 1. Diffractogram for the different alloys (a) TiCr_{1.1}V_{0.9} alloy, (b) TiCr_{1.1}V_{0.9}Zr_{0.2} alloy (c) TiCr_{1.1}V_{0.7}Zr_{0.4} alloy.
The diffractogram for the Ti\textsubscript{1.1}V\textsubscript{0.9}Zr\textsubscript{0.2} alloy can be seen in Figure 1(b). Here a double-phase can be observed; one which is a bcc phase and the other a Laves phase with a cubic-type C15 compound ZrCr\textsubscript{2}, which arises from the addition of Zr. This result corresponds with those of K. Shashikala et al [5] who added Zr as a substitute for Ti in the alloy TiCrV.

The formation and stability of this Laves phase depends upon the ideal ratio of atomic radii between neighbouring atoms A and B being \( r_A / r_B = \sqrt{3} / \sqrt{2} = 1.225 \). As such, it is possible to experimentally obtain a ratio between 1.06 and 1.67. This property corresponds with the atoms geometrical compression factor since they are able to contract and expand as they approach the ideal ratio [6]. For this reason, the geometrical rule is important for predicting the appearance of the Laves phases.

Since the pairs of elements approach the ideal ratio \( \approx 1.225 (R_{Zr} / R_{Cr} = 1.26) \), it can be expected that the alloys in the present study form Laves phases. The atomic ratio for Zr is 1.60Å and for Cr it is 1.27Å.

The diffractogram for the Ti\textsubscript{1.1}V\textsubscript{0.7}Zr\textsubscript{0.4} alloy can be seen in Figure 1(c) where the appearance and growth of a new peak corresponding with the Laves phase C15 can be seen. This is due to increasing the amount of Zr in the alloy as explained above.

The lattice parameters for each of the alloys are shown in Table 1 along with the phases that occurred for each one.

| Alloy              | Phases          | Lattice parameter (Å) | Capacity (%wt) |
|--------------------|-----------------|-----------------------|----------------|
| Ti\textsubscript{1.1}V\textsubscript{0.9} | BCC             | 3.06                  | 3.6            |
| Ti\textsubscript{1.1}V\textsubscript{0.9}Zr\textsubscript{0.2} | BCC             | 3.14                  | 3.0            |
|                    | Laves phase C15 | 7.19                  |                |
| Ti\textsubscript{1.1}V\textsubscript{0.7}Zr\textsubscript{0.4} | BCC             | 3.18                  | 2.0            |
|                    | Laves phase C15 | 8.03                  |                |

### 3.2. Absorption properties

Figures 2 and 3 show the time taken for hydrogen to be taken up and the storage capacity of each alloy. Figure 2(a) for the Ti\textsubscript{1.1}V\textsubscript{0.9} alloy shows a high sorption capacity of 3.6%wt (% percentage by weight), however, the process takes approximately 58 minutes before hydrogenation begins.

This is characteristic of these types of alloys that produce a heavy oxide layer that cannot be easily removed without using high temperatures. Such a process of removing any kind of surface water or oxidation is called activation and is carried out in a vacuum at approximately 350°C during an hour. Even so, the oxide layer remains intact and could be removed at higher temperatures but with the result that the sample carrier would be destroyed. The absorption process begins at the point at which the hydrogen penetrates the oxide layer.

In Figures 2(b) the hydrogen absorption capacity decrease to 3.0%wt for the Ti\textsubscript{1.1}V\textsubscript{0.9}Zr\textsubscript{0.2} alloy and Figure 3 the hydrogenation time decreases significantly to 2.0%wt for the Ti\textsubscript{1.1}V\textsubscript{0.7}Zr\textsubscript{0.4} for to a matter of minutes due to the formation of laves phases thanks to increasing the amount of Zr.

The activation process is the same for all of the samples with the difference that the formation of the laves phases acts as a catalyst for the hydrogen reaction with the surface of the metal. Given that these phases make up a small percentage of the main matrix and their mechanical properties are weaker than those of the preponderant alloy TiCrV, the hydrogen is first diffused in this phase creating preferred pathways or short-circuits until the main bcc structure is broken. This process, which concurs with the results reported by [7], occurs in a question of minutes until the alloy is saturated with hydrogen.

However, the hydrogen uptake rate drops from 3.8%wt to 3.0% and 2.0%wt respectively. This is due to the fact that the Laves phases increase their content and compete with the bcc phase, and in so doing impede the number of available places that can serve as hydrogen storage. This matches the studies by [7,8].
4. Conclusions
Substituting Zr for V in the alloy TiCrV was studied. It was verified that the compounds TiCr$_{1.1}$V$_{0.9}$Zr$_{0.2}$ and TiCr$_{1.1}$V$_{0.7}$Zr$_{0.4}$ give rise to a double-phase structure made up of primarily a bcc structure and a smaller Laves C15 cubic-type structure. The appearance of a Laves C15 phase in the TiCrV alloys can be controlled by varying the number of Zr and V atoms.

Substituting Zr augments the lattice parameters and decreases the hydrogen absorption capacity due to the increase in laves phase structures that compete with the bcc structures. The laves phase acts as a catalyst for the absorption reaction.

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