

Metal hydrides with BCC structure: Advantages and challenges

A. Martínez - Amariz^{1,3}, Dario Peña², and A. Gonzalez –Estrada², Quesada-Plata-F³

¹ Universidad de Santander, Facultad de Ingeniería, Grupo de Investigación Nuevas Tecnologías, Bucaramanga, Colombia.

² Universidad Industrial de Santander, Facultad de Ingeniería, Escuela de Ingeniería Mecánica, Bucaramanga Colombia

² Universidad Industrial de Santander, Facultad de Ingeniería, Escuela de Ingeniería Metalúrgica, Bucaramanga Colombia

³ Grupo de Investigación en Ciencias Básicas Aplicadas, Departamento de Ciencias Básicas, Unidades Tecnológicas de Santander, Bucaramanga Colombia

E-mail: alejandrom@udes.edu.co

Abstract. Metal hydrides are considered an easy and safe way to store hydrogen. Storage is one of the keys to the large-scale implementation of the so-called Hydrogen Economy, which will undoubtedly revolutionize the new vision of sustainable development towards a more environmentally friendly world. This paper presents a general review of some alloys based on TiCrV and TiCrVZr showing their advantages and challenges that must be developed for their implementation. The capacity of absorption and desorption as a function of time is shown using a Sieverts type device, the structure is studied by means of XRD as well as its morphology by means of Scanning Electron Microscopy. In the study shows a high capacity of absorption of hydrogen although its desorption at room temperature is not optimal.

Introduction

The hydrogen economy is reaching interesting levels of maturity that positions this energy sector as a serious candidate to replace fossil fuels, with important applications such as power generation, mobile and stationary [1]. The hydrogen economy consists of several stages for its implementation, the first is the production of hydrogen that is currently developed by reforming natural gas; in this process natural gas reacts with water vapor at high temperatures between 1500 - 1700 ° C and pressures between 20-30 bar producing large amounts of CO₂ [2]. However, with the accelerated development of renewable energies such as solar, wind and others, a large production of hydrogen is expected at low cost through the electrolysis of water, with zero CO₂ emissions that could cover the demand [3-4]

On the other hand, proposals are already being developed to produce hydrogen with the surplus of nuclear and hydroelectric energy in times where the demand is lower, with this it is sought that this production process significantly lowers the costs to become completely viable [5-6] The second stage

consists of the storage of hydrogen, which can be developed in small and large scale and which is undoubtedly one of the keys for the implementation of the hydrogen economy.

The methods for storage are conceptually simple and some are in commercialization stage, among which the compressed hydrogen stand out in pressurized tanks that use special steels reinforced with carbon fiber and reach maximum pressures of 70 bar [7]. The way of storage under pressure is being used in commercial cars that use fuel cells only one of the problems is the low storage capacity of this gas because there is a maximum that can be compressed without causing any damage to the structure of tank.

Another type of hydrogen storage are metal hydrides that have a high storage capacity depending on their structure. Many of the compounds that are formed are due to the absorption of hydrogen inside the metallic matrix, in a first phase the hydrogen dissolves inside the alloy forming a solid solution (α phase). When the concentration of hydrogen and pressure increases, the formation of the hydride phase begins (β phase) until it reaches its maximum storage value [8]. This process can be studied from the thermodynamics of pressure curves isothermal composition (P-C-T), where the phases coexist (phase $\alpha + \beta$) showing a constant line or a "plate". This type of reaction is exothermic in the absorption process releasing a large amount of energy and endothermic in the process of desorption of hydrogen, ie it is necessary to introduce energy to release hydrogen [9]. The reaction can be written as:



Among the metal hydrides are the Mg-based alloys that have a high gravimetric storage capacity around the (7.6 wt%) and high volumetric capacity (110g / L), in addition to its low cost and abundance these characteristics make it very attractive. However, its implementation on a commercial scale is restricted due to the poor absorption / desorption kinetics, ie the time to reach the phase ($\alpha + \beta$) can take several hours added to the high enthalpy necessary for the absorption / desorption process reflected in high temperatures around 250-350 ° C [10]. However, great efforts are being developed to improve these barriers such as the use of nanocatalysts, surface modification, addition of other intermetallic elements, nanocomposites, amorphization among others [11].

The other promising hydrides are hydrides based on transition or intermetallic metals that can be classified according to their stoichiometry as AB₅ (eg LaNi₅), AB₂ (eg TiFe₂), A₂B (eg Sb₂Ti), AB (eg Ti-Fe) and Cubic-centered body structures called hydrides in bcc-based solid solution (eg TiCrV) [12]. These alloys have advantages as hydride formers since the hydrogen can be stored in the solid state at room temperature, between (25-40 ° C) and moderate pressures which provide a high safety when compared to the pressures used in the tanks pressurized and liquid hydrogen. The key is that in these structures you can pack more hydrogen atoms inside the crystal lattice in the same volume used to store it in liquid and gaseous form. It is estimated that the storage capacity goes between the ranges of (1.4 - 4.2 wt%), this from the point of view for commercial applications is high. However, it has certain disadvantages such as the high energy rate that occurs at the time of absorption that decreases the performance in the next cycle due to the high temperature that occurs, on the other hand, the desorption process, although it is fast do not desorb all the stored hydrogen due to the formation of several hydride phases that are very stable at room temperature and only expel hydrogen when the temperature is increased [13-14].

In this paper, advantages and challenges are exposed that must be taken into account in alloys based on the BCC structure from the point of view of the synthesis and characterization process.

1. Synthesis processes

The capacity of absorption of hydrogen is strongly dependent on the methods used for the synthesis of alloys, in many works methods of synthesis are exposed for the development of these alloys one of them is by means of fusion to arc.

The fusion to arc allows to obtain a homogeneous structure because it allows the homogenization of the alloy and free from contamination by its controlled atmosphere, authors like [15, 16] have synthesized homogeneous structures and that have been verified by X-ray diffraction this structure presents a single phase bcc.

One of the disadvantages is that the elements used in this process must be of high purity (> 99.95). This fact makes costs expensive because these materials are expensive if they are to be used for commercial applications, however, some researchers are using combined metals as FeV or commercial Fe that could become cheaper without diminishing its quality [17].

The other method is based on mechanical alloy (MA) using a ball milling, this method is widely used to produce alloys with bcc structure where a high energy is provided by the collisions of the spheres that allow a fracture of the materials until obtaining a mechanical alloy type fusion..

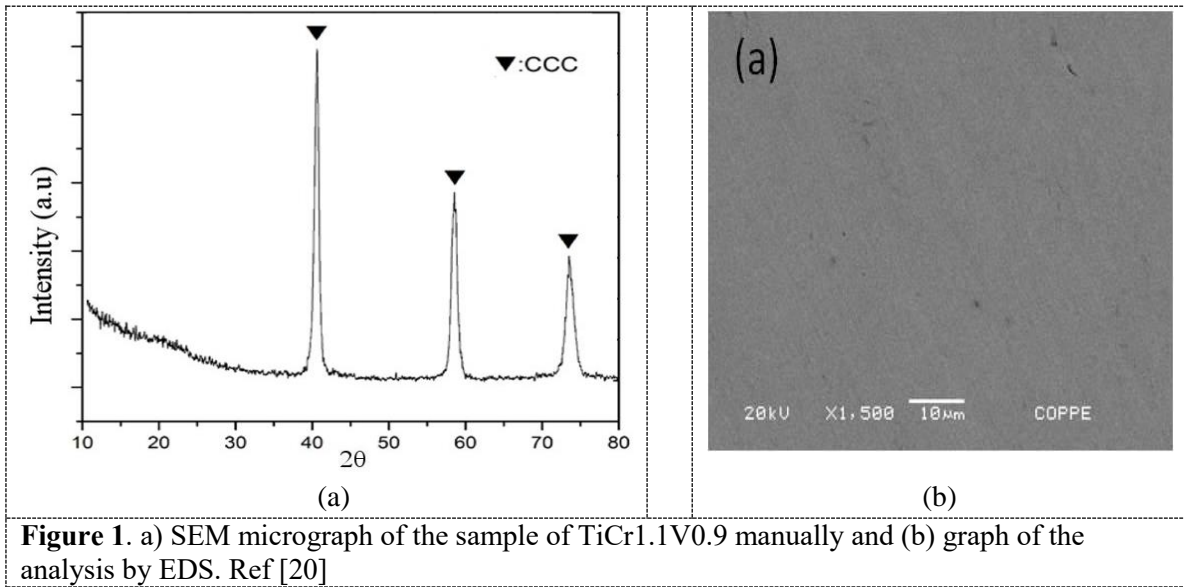
For this purpose, high energy planetary mills and steel or tungsten spheres are used. This grinding process is carried out for several hours until the desired structure is obtained, as demonstrated by the authors [18], allowing alloys to be obtained at low cost compared to those produced by fusion to arch. From the point of view of the absorption property, the mechano synthesis can improve the reaction kinetics allowing the absorption times to be shorter because there are more surface areas free of any type of contamination [18].

One of the disadvantages lies in the fact of contamination by the spheres of the mill in addition to the amorphization of the alloy [19]. Special care must be taken in oxygen contamination since these manometric materials lose all their absorption capacity when they are oxidized.

2. Hydrogen absorption processes

Absorption processes are determined by several factors that may favor or affect their performance. One lies in its microstructure in which the crystallographic structure allows to obtain a high storage capacity as presented by [14, 16] in which a single phase formation with bcc structure with a storage capacity of 4.2 wt% is observed and 3.6 wt% respectively. Figure 1 shows the diffractogram as well as the micrograph of the alloy TiCr_{1.1}V_{0.9} of [20], this is achieved due to the fusion process described above and that allows an excellent solubility of the elements. Simulations are being developed in recent years to more accurately predict the structures that can originate, such is the case of the studies developed by [21] in which software using the CALPHAD method is used to determine ternary diagrams based on thermodynamic data experimental.

This tool is powerful because it saves time and money in order to develop new alloys for the storage of hydrogen



However, there is a difficulty that lies in the initial time in which the alloy begins to absorb hydrogen, this is because the alloys based on TiCrV have three stages to reach their maximum capacity, in the incubation stage the pressure it remains constant and there is no absorption of hydrogen in the metal. This phenomenon is due to the effect of passivation of the surface, related by the existence of oxide layers and impurities on the surface of the material and by the filling of the sites corresponding to the solid solution.

In the absorption stage the reaction kinetics increases due to the fact that the effects caused by pressure and temperature promote the rupture of the oxide layers, generating the absorption of hydrogen, which is measured through the pressure variations in function weather. Finally, in the equilibrium stage, the metal can not absorb more hydrogen at a given temperature, remaining at a constant value, that is, the metal is supersaturated with hydrogen inside it.

These times can take very long periods of time like the one presented by [16] and shown in figure 2, where each of the stages of the process is observed, this from the technological point of view is not practical because it requires less time initial absorption

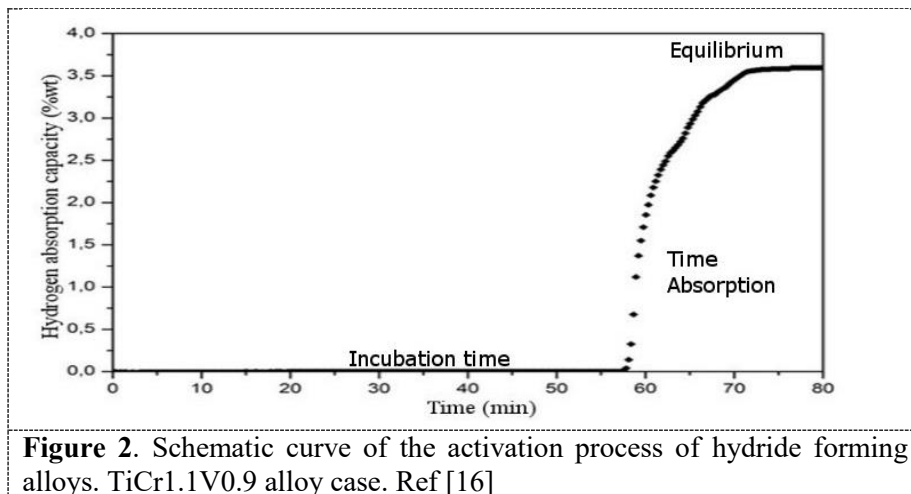


Figure 2. Schematic curve of the activation process of hydride forming alloys. TiCr1.1V0.9 alloy case. Ref [16]

Currently, new alloys are being developed that allow rapid kinetics of hydrogen absorption based on the formation of more than two structures, as in the case of [22] in which the addition of Zr allows the formation of a bcc structure and another structure called phase Laves, this allows great advantages because the washing phase for being mechanically more fragile causes a rapid absorption allowing a rupture of the material and more layers without oxide of the bcc structure are exposed allowing the incubation time to significantly decrease or be eliminated as observed in figure 3, and corroborated by X-ray diffraction.

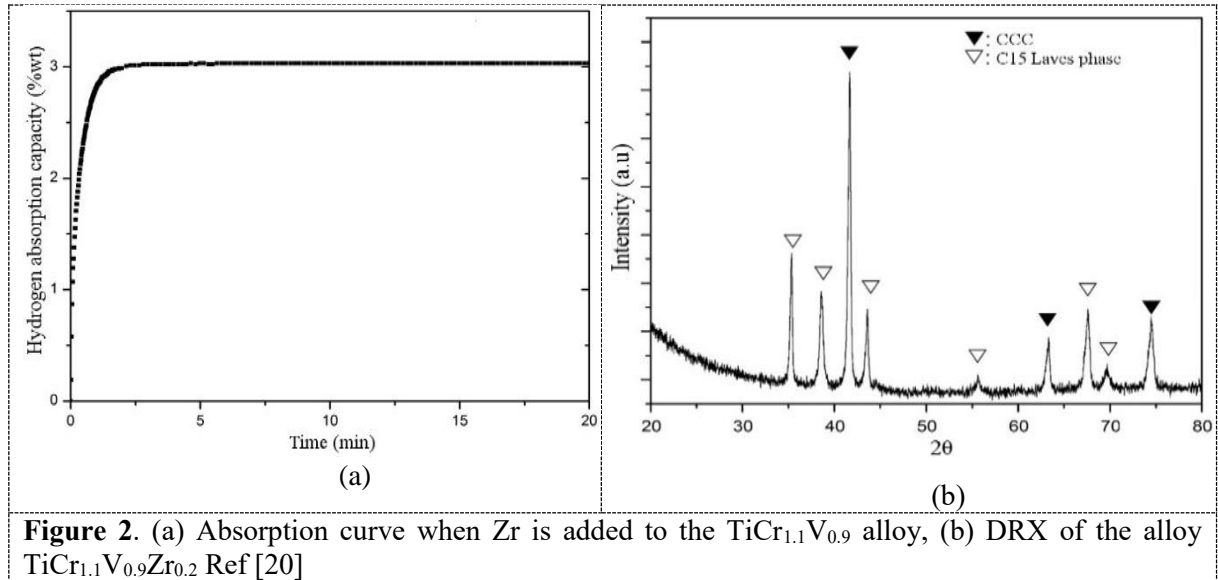


Figure 2. (a) Absorption curve when Zr is added to the $\text{TiCr}_{1.1}\text{V}_{0.9}$ alloy, (b) DRX of the alloy $\text{TiCr}_{1.1}\text{V}_{0.9}\text{Zr}_{0.2}$ Ref [20]

The formation and stability of this Laves phase depends upon the ideal ratio of atomic radii between neighboring 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 [22]. 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 $\approx 1,225$ ($R_{\text{Zr}} / R_{\text{Cr}} = 1.26$), it can be expected that the alloys in the present study form Laves phases. The atomic ratio for Zr is 1.60\AA and for Cr it is 1.27\AA .

However, the hydrogen uptake rate drops from $3.6\%wt$ to 3.0% . 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 [20].

3. Conclusions

There are challenges to achieve the proposed objectives so that alloys with a bcc type structure are strong candidates for the storage of hydrogen in a safe manner and with a good performance for this, the efforts are focusing on two fundamental aspects.

The first lies in the synthesis process which requires it to be efficient and low cost to be considered as is the process of fusion to arc that allows to obtain homogeneous structures, the other process that is even more economical is the mechanical grinding. It can be used to produce nano alloys on a large scale.

The use of thermodynamic simulation is relevant because it allows to study and design alloys based on ternary diagrams, this contributes to a saving both in the experimental times and in the total costs of the same. Undoubtedly the simulation will open a new window in this field of research.

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