Effect of adding ZrM (M = Fe, Ni) intermetallic compounds on the hydrogen absorption/desorption properties of TiCr$_{1.1}$V$_{0.9}$ alloy

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ABSTRACT

In this paper, the effect of intermetallic compounds Zr$_2$Fe and Zr$_7$Ni$_{10}$ on the microstructure and first hydrogenation kinetic of TiCr$_{1.1}$V$_{0.9}$ alloy is reported. Samples were synthesized by arc melting separately and then 5% of each intermetallic was co-melt with TiCr$_{1.1}$V$_{0.9}$ alloy. First hydrogenation of all alloys was performed at room temperature under 2.0 MPa of hydrogen. Kinetics and absorption capacities were measured at room temperature, by using apparatus type sieverts. Results indicate that the addition of the intermetallic has an enhancing effect on the kinetic reaction without further modification of hydrogen storage capacities, going from 3.6 wt.% for as-cast alloy, to 3.61 wt.% for alloys +5 wt.% intermetallic. On the other hand, the structure and microstructural analysis were carried out by X-ray diffraction and scanning electron microscopy, respectively. These results show conservation of the structure in the body-centered cubic, and two additional minor phase formations: C14 laves phase for both alloys, and an additional Ti$_2$Ni phase for the TiCr$_{1.1}$V$_{0.9}$ + 5% Zr$_7$Ni$_{10}$ alloy. Finally, the thermal stabilization of the sample was determined by using differential scanning calorimetry. The results show two types of hydrides that form trapped in different clamping sites with different energies.

1. Introduction

Current dependence on fossil fuels has serious drawbacks, such as pollution and long-term climate changes. Due to this, alternative energies are gaining ground. Hydrogen is considered as a sustainable and reliable energy carrier, and one of the alternatives as a clean and efficient source [1]. However, to use it commercially, hydrogen must overcome the challenges of being stored efficiently. Transition metals have a high affinity for hydrogen, forming metal hydrides, which makes them attractive for hydrogen storage in the solid-state. The way hydrides store hydrogen makes them safer when compared to other techniques such as cryogenics and pressurized tanks [2]. The TiVCr-based system has been extensively studied [3, 4, 5, 6]. The TiVCr-based system is considered highly promising for hydrogen storage, due to its body-centered cubic structure, which facilitates its diffusion under moderate temperature and pressure conditions [7], and also has a higher storage capacity when compared to traditional systems like AB$_x$ (x = 1, 2, 5) [8]. Ti–Cr–V alloy system is generally difficult to activate, the reversible capacity is lower and shows a long incubation time during the first hydrogenation [9, 10]. The TiCr$_{1.1}$V$_{0.9}$ alloy based on this system has been studied by [11] with advantages such as its high hydrogen storage capacity (3.55 wt.%) at moderate temperatures (298 K). This allows it to be considered as an optimal alternative to be used in fuel cells, however, its poor hydrogen desorption capacity at room temperature presents a difficulty.

Intermetallic hydrides showing a higher hydrogen storage capacity, usually form a BCC structure by solid solution. However, they have some limitations such as the low desorption capacity, mainly at moderate temperatures, the slow reaction of hydrogen with the microstructure, in addition to its high hardness, which prevents it from improving its performance [12]. Akiba and Iba investigated ternary alloys such Ti–V–Mn and TiCrV, which have a structure denoted Laves phase related BCC solid solution, capable of absorbing large amounts of hydrogen at room temperature, stability, cyclability and fast kinetics [12, 13, 14]. Chen LX et al demonstrated that the Laves phases act as a mechanism that increases the acceleration in the absorption/desorption kinetics of the BCC solid solution phase [13]. Equally intermetallic compounds have been proposed as catalysts to increase the kinetics and hydrogen absorption capacity in TiCrV alloys [15].

The objective of this work is to study the effect of adding several intermetallic compounds like Zr$_2$Fe and Zr$_7$Ni$_{10}$ into the structure, and the properties of absorption/desorption of TiCr$_{1.1}$V$_{0.9}$ alloy.
2. Experimental procedure

Synthesis- All the raw elements were purchased from Alfa-Aesar and used without further purification. TiCr1.1V0.9 alloy was chosen as the starting composition due to its maximum hydrogen storage capacity reported before [11]. Zr2Fe and Zr7Ni10 were melted separately, and then 5% of each intermetallic were co-melt with TiCr1.1V0.9 alloy. All samples were developed using the technique by arc melting in argon atmosphere and each sample was remelted at least three times to ensure a good homogeneity of the pieces.

Crystal structure and microstructure analysis- Crystal structure and lattice parameters were studied by X-ray diffraction (XRD) using a Shimadzu 5000 diffractometer with Cu Kα radiation. Crystal structure parameters and local compositions were analyzed with Energy-dispersive X-ray spectroscopy (EDX, THERMO/NORAN). Samples were pulverized using a steel mortar with an average particle size/length/diameter of 100 μm.

Activation procedure- 1.08 g of the alloys previously broken with a steel mortar in the air, were introduced into the autoclave. The activation process was carried out by placing the sample in the autoclave to maintain a vacuum for 2 h at 573 K using a turbomolecular pump that allows removing any type of moisture and oxides present on the surface. Subsequently, they were allowed to cool down until they reached room temperature, to start the absorption process with the Sieverts type apparatus. Each sample after the absorption and desorption process was again subjected to the previously described process, with the aim of removing all the remaining hydrogen.

Hydrogen absorption and desorption capacities- The hydrogen absorption/desorption properties of the as-cast sample were measured with a Sievert’s type gas absorption analysis device (PCT pro-2000), at different temperatures (300 K, 313 K, and 373 K) and 2.0 MPa pressure considering that all the samples were previously activated.

Thermal stabilization- The thermal stabilization of the samples was determined by using differential scanning calorimetry (DSC). This analysis was carried out at a heating rate of 10 °C/min in an argon atmosphere. The working temperatures were between room temperature and 900 K, and the flowing gas Ar was used as the carrier with the rate of 20 ml/min. The samples were obtained after being hydrogenated in the apparatus type Sievert under a pressure of 2.0 MPa.

3. Results and discussion

Crystal structure- X-ray diffraction pattern of TiCr1.1V0.9 alloy in as-cast state is shown in Figure 1(a). It is clear from the Fig that the as-cast alloy has body-centered cubic (bcc) phase. This Fig shows a small peak that is formed due to Ti is not completely solubilized in the matrix. This Ti peak is known as an α-titanium phase [16]. The addition of 5% Zr2Fe and 5% Zr7Ni10 are shown in Figures 1(b) and 1(c), respectively. For those, the conservation of the structure in the body-centered cubic it is clear, however, two additional minor phases were observed. Analysis of the patterns show that for both intermetallic compounds a C14 laves phase is formed. Nevertheless, for the TiCr1.1V0.9 + 5% Zr7Ni10 alloy a third phase is formed, corresponding to the Ti2Ni phase.

Lattice parameters for each alloy were evaluated by Rietveld refinement and reported in Table 1. In this table a decrease in the parameter of the bcc structure is observed, mainly due to the diffusion of titanium in the intergranular phase.

Figure 2 shows the X-ray patterns of the hydrogenated samples. The formation of two hydride phases can be seen, which is characteristic of alloys with a BCC structure of TiCrV alloys [17], which changes from bcc to fcc structure after the first absorption cycle [18]. The formation of the hydride TiCr1.8H5.3 with fcc structure is observed, the characteristic of it is that the content of V that presents a bcc structure dissolves and precipitates in the TiCr1.8H5.3 phase during hydrogenation, this process was studied by [17]. Likewise, the formation of the hydride TiH2 coinciding simultaneously with a bcc structure is observed, this is formed after the hydride is saturated with hydrogen. The first hydride is formed at low pressures and the second at high pressures. This phenomenon is also studied in detail by [19].

Microstructures- The compounds obtained by co-melting of TiCr1.1V0.9 + 5% Zr7Ni10 and TiCr1.1V0.9 + 5% Zr2Fe alloys, have mainly

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Table 1. Phase structure of the alloys.

| ALLOY          | Phase       | % Phase | Lattice Parameter (Å) |
|----------------|-------------|---------|-----------------------|
| TiCr1.1V0.9    | BCC         | 100     | a = 3.06              |
| TiCr1.1V0.9 + 5%Zr2Fe | BCC     | 99.6    | a = 3.05, c = 5.37   |
| TiCr1.1V0.9 + 5%Zr7Ni10 | BCC   | 9.5     | a = 3.06, c = 4.89   |

Figure 1. XRD pattern of the as-cast alloy a) TiCr1.1V0.9, b) TiCr1.1V0.9 + 5%Zr2Fe, c) TiCr1.1V0.9 + 5%Zr7Ni10.
two types of phases. All alloys are made of a gray predominant phase along with a bright phase, the gray phase will be thereafter called matrix. The microstructures of the samples are presented in Figure 3. TiCr1.1V0.9 microstructure is showed as a reference in Figure 3(a). Figure 3(b) shows a predominant phase matrix corresponding to body-centered cubic TiCrV alloy and zirconium-rich intergranular phase and nickel. Figure 3(c) shows zirconium-rich intergranular phase and iron. The intergranular phases are distributed evenly and draw a microstructure with a characteristic cell size of 50 μm. The relative abundance of the phases corresponds to the mass ratio of 5% Zr7Ni10 and 5% Zr2Fe. This over-abundance is mainly due to the diffusion of titanium atoms. During cooling, the bcc phase first solidifies to form a three-dimensional structure and later the rest of the liquid solidifies in Laves phase as the temperature in the alloy decreases [20]. This makes it possible to explain that the addition of intermetallic facilitates the hydrogenation process, since Zr is present mainly in the intergranular phase, and has a great hydrogen affinity. These results are similar to and explained by [20] when the intermetallic Zr7Ni10 is added to the TiFe alloy as co-melting.

Figure 3. Microstructure of the samples, (a) TiCr1.1V0.9, (b) TiCr1.1V0.9 + 5% Zr7Ni10, (c) TiCr1.1V0.9 + 5% Zr2Fe.
Table 2. Composition of bcc solid solution of the different alloy.

| SAMPLE                      | Ti   | Cr   | V    | Zr   | Ni   | Fe   |
|-----------------------------|------|------|------|------|------|------|
| TiCr$_{1.1}$V$_{0.9}$       | 36,38| 43,27| 20,35| -    | -    | -    |
| TiCr$_{1.1}$V$_{0.9}$ + 5% Zr$_7$Ni$_{10}$ Matrix bcc | 33,88| 36,00| 30,12| -    | -    | -    |
|                            | 46,20| 18,38| 10,47| 12,45| 12,49| -    |
| TiCr$_{1.1}$V$_{0.9}$ + 5%Zr$_2$Fe Matrix bcc | 33,30| 35,74| 30,24| -    | -    | 0,71 |
|                            | 40,32| 26,82| 15,29| 15,42| -    | 2,15 |

Figure 4. Absorption cycle at different temperatures for TiCr$_{1.1}$V$_{0.9}$ + 5% Zr$_7$Ni$_{10}$ and $P = 2.0$ MPa.

Figure 5. Absorption cycle at different temperatures for TiCr$_{1.1}$V$_{0.9}$, TiCr$_{1.1}$V$_{0.9}$ + 5%Zr$_2$Fe alloys and $P = 2.0$ MPa.
The chemical composition of the bcc solid solution plus intermetallic alloys was evaluated by EDX analysis. The results are shown in Table 2.

Absorption capacities and kinetics—Figure 4 shows the hydrogen absorption kinetics curves for TiCr$_{1.1}$V$_{0.9}$ and TiCr$_{1.1}$V$_{0.9}$+5% Zr$_7$Ni$_{10}$ alloys, samples were measured at 300 K, 313 K, and 373 K under 2.0 MPa H$_2$. The first hydrogen absorption cycle for TiCr$_{1.1}$V$_{0.9}$ at room temperature has an incubation time of approximately 9 min due to the oxide layer which is on the surface. This composition reaches a maximum capacity of hydrogen 3.60 wt. % in approximately 3 min. When 5% of Zr$_7$Ni$_{10}$ as co-melting is added, the time of incubation decays to 30 s in the first cycle and achieved a maximum capacity of 3.61 wt.% in 2 min. This indicates that the intermetallic improves the kinetics of the reaction due to the formation of the Laves phase. This type of formation, due to its low hardness characteristic, allows easy pulverization when compared to the BCC phase, which has a high hardness. This is due to the synergistic effect between the C14 phase and BCC, as well as the nature of the catalytic surface. That is, this phenomenon is due to the change in the contact area of the primary phase with the secondary phase, causing this synergistic effect. This phenomenon was studied in detail by [21].

Therefore, more hydrogen can penetrate into the alloy bulk through and lattice parameter increased, this property is discussed by Bououdina et al [22]. The large absorption capacity in the first cycle is mainly due to the difference in atomic radii (Ti = 1.46 Å, V = 1.35 Å, Cr = 1.28 Å)
Figure 8. Desorption tests by DSC with the different hydrides. Exothermic peaks of (a) TiCr1.1V0.9 alloy, (b) TiCr1.1V0.9 + 5%Zr2Fe alloy, (c) TiCr1.1V0.9 + 5% Zr2Fe alloy.

which means that the alloy has a larger lattice constant and therefore wider crystal planes spacing. However, when increasing of temperature, absorption capacity drops from 2.0 wt.% to 0.75 wt.% a 313 K and 373 K respectively.

The decrease in absorption capacity is characteristic of hydrogen-metal systems with increasing temperature, as shown by Xuebin et al. [23] in the alloy Ti–20Cr–12Mn–24V–5Fe where the pressure of hydrogen absorption-desorption plateau increasing with increasing temperature. Since the ratio between the pressure of absorption and desorption is related to the Gibbs free energy, \( \Delta G_f = \Delta G_d = RT \ln \left( \frac{p_f}{p_d} \right) \) that decrease while temperature increases where \( p_f \) is the pressure of hydride formation and \( p_d \) is desorption pressure.

Figure 5 shows the alloy’s behavior when \( +5\%\text{Zr}_2\text{Fe} \) is added. Here, it’s possible to observe a non-incubation time in the first cycle and a maximum hydrogen storage capacity of 3.61 wt.% in 2 min. The capacity drops to 2.0 wt.% at 313 K and to 0.75 wt.% at 373 K. However, a better performance can be observed in the absorption capacity compared with the \( \text{Zr}_7\text{Ni}_{10} \).

Desorption capacities- Figures 6 and 7 show the desorption curves for TiCr1.1V0.9 + 5\%Zr7Ni10 and TiCr1.1V0.9 + 5\%Zr2Fe alloys at different temperatures, respectively. Here, it’s possible to observe that at room temperature the desorption capacity is low in both alloys. This is mainly due to the stability of the hydride at room temperature caused by different metal-hydrogen bonds. The Ti–H bond is stronger than the Cr–H bond at these temperatures, therefore, as there are more atoms of Ti less hydrogen is released.

However, the desorption capacity for both alloys increases with temperature. In Figure 6 the behavior for TiCr1.1V0.9 + 5\%Zr7Ni10 alloy is presented. For this alloy, the desorption capacities are 0.3 wt.% y 0.26 wt.% at 300 K, 313 K y 373 K, respectively.

Figure 7 shows the desorption capacities for TiCr1.1V0.9 + 5\%Zr2Fe alloy at different temperatures. For this alloy, the desorption is 0.3 wt.% y 0.8 wt.% at 0.63 wt. % at 300 K, 313 K y 373 K, respectively. This indicates that the TiCr1.1H0.3 hydride, showed better performance at moderate temperatures since the TiH2 hydride destabilizes at higher temperatures up to 653 K. These phenomena were verified by HC Lin et al. [19] in the TiVCr and Ti0.8Cr1.2V alloy.

Hydrogen desorption study using Differential Scanning Calorimetry (DSC)- Thermal stabilization of the samples was determined by using differential scanning calorimetry (DSC). The results are shown in Figure 8, where it’s possible to observe the different endothermic peaks for released hydrogen. Two types of hydrides are observed that form trapped in different clamping sites with different energies. This matches the XRD analysis results. In Figure 8(a) the TiH2 hydride is released above 750 K, however, when the intermetallic is added, the second hydride is released at lower temperature (620 K). This implies a destabilization for the TiH2 hydride, this phenomenon was also observed by Basak [24].

4. Conclusions

In the present study, hydrogen storage properties of TiCr1.1V0.9 + 5 wt.% Zr7Ni10 and TiCr1.1V0.9 + 5 wt.% Zr2Fe alloys, have been studied. All the alloys showed a phase bcc, laves phase, and the TiCr1.1V0.9 + 5 wt.% Zr7Ni10 shows a third phase corresponding to Ti2Ni phase.

The kinetic studies show that hydrogen absorption takes place in an incubation time of 30 s in the first cycle for of TiCr1.1V0.9 + 5 wt.% Zr7Ni10 and achieved a maximum capacity of 3.61 wt.% in 2 min. While for the TiCr1.1V0.9 + 5 wt.% Zr2Fe alloys, hydrogen absorption takes place without incubation time, and reaches a maximum hydrogen absorption capacity of 3.61 wt.% in 2 min. This implies that intermetallic act as reaction accelerator that increase the absorption kinetics due to the formation of the Laves phase, allowing the alloy to become more brittle and create a fresh surface for the entrance of hydrogen.

Also, Zr7Ni10 and Zr2Fe intermetallic alloys in the TiCr1.1V0.9 allow an easy activation in the first absorption cycle, eliminating the need for alloy exposure to different hydrogenation processes at high pressures to activate.

Declarations

Author contribution statement

A. Martínez-Amariza, D. Bellon: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data included in article.supplementary material/referenced in article.
Declaration of interests statement

The authors declare no conflict of interest.

Additional information

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