

Article

Microstructure and First Hydrogenation Properties of Individual Phases in TiFe + 12 wt.% ZrV₂ Alloy

Daniela Bellon Monsalve ^{1,2,*} , Elena Ulate-Kolitsky ³ , Jorge M. Cubero-Sesin ⁴ ,
Alejandro-David Martínez-Amariz ²  and Jacques Huot ^{1,*} 

¹ Hydrogen Research Institute, Université Du Québec à Trois-Rivières, Québec, QC G9A 5H7, Canada

² Facultad de Ingenierías y Tecnologías, Instituto de Investigación Xerira, Universidad de Santander, Bucaramanga 680003, Colombia; alejandrom@udes.edu.co

³ Centre de Métallurgie du Québec, 3095 Rue Westinghouse Parc Industriel Des Hautes-Forges, Trois-Rivières, Québec, QC G9A 5E1, Canada; elena.rosemarie.ulate.kolitsky@cegeptr.qc.ca

⁴ Centro de Investigación y Extensión en Materiales, Escuela de Ciencia e Ingeniería de los Materiales, Instituto Tecnológico de Costa Rica, Cartago 159-7050, Costa Rica; jcubero@itcr.ac.cr

* Correspondence: daniela.bellon@uqtr.ca (D.B.M.); jacques.huot@uqtr.ca (J.H.)

Abstract: This study investigates the microstructure and first hydrogenation properties of Fe₅₂Ti₄₀Zr₃V₅ and Fe₃₇Ti₄₄Zr₉V₁₀ alloys, which are individual phases present in the as-cast TiFe + 12 wt.% ZrV₂ alloy (parent alloy). The parent alloy exhibited fast first hydrogenation kinetics due to the interplay of these two phases. Our objective is to study the hydrogen storage behavior of these individual phases. The samples were synthesized by arc melting and characterized by X-ray diffraction, scanning electron microscopy, and energy-dispersive spectroscopy. The results show that when these alloys are melted separately, they do not exhibit the same phase composition as in the parent alloy, indicating a metastable state under our synthesis conditions, which significantly impacts their hydrogen storage behavior. Hydrogenation capacity was measured using a homemade Sieverts apparatus. Both alloys demonstrated excellent first hydrogenation kinetics, with an absorption capacity of 0.9 wt.% for the Fe₅₂Ti₄₀Zr₃V₅ alloy and 2.3 wt.% for Fe₃₇Ti₄₄Zr₉V₁₀ alloy. Our key finding is that the final crystal structure of multi-element alloys is highly dependent on the synthesis method.

Keywords: metal hydrides; TiFe alloy; hydrogen storage; first hydrogenation; microstructure



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1. Introduction

The transition to renewable energy sources presents several challenges, including the production, storage, and distribution of energy. Hydrogen, as a versatile energy carrier, plays a crucial role in this transition due to its potential for high energy density and low environmental impact [1,2]. However, a major barrier to the widespread adoption of hydrogen energy systems is the development of safe, efficient, and cost-effective hydrogen storage methods [3]. Currently, high-pressure and liquid hydrogen storage methods are the most developed and widely used technologies; however, they present significant safety risks and demand substantial energy consumption [4]. Therefore, focus has shifted to innovative materials and approaches such as magnesium-based alloys, which demonstrate high hydrogen storage capacity and improve their properties through alloying with metals like rare earth metals, carbon materials, and others [5]. High-entropy alloys, containing five or more elements, show significant potential in which the control of the mixture's configurational entropy and other parameters have allowed the prediction and control of phases formed in different alloy compositions and systems [6,7]. Amorphous materials, which lack a crystalline structure, also stand out for their long-range disordered atomic structure, which allows a wider interstitial configuration diversity and provide hydrogen with more types of occupation sites [8]. Similarly, composite materials that combine different types of

hydrogen storage materials, such as metal hydrides with polymers or carbon-based materials, exhibit optimized performance due to its ability to effectively control and prevent surface contamination from oxygen and moisture [9]. Metal-organic frameworks (MOFs) are being investigated for their high surface area and the high tunability brought by the co-existence of organic and inorganic units that allows to improve the hydrogen storage through various strategies [10,11], while liquid organic hydrogen carriers (LOHCs) provide a novel method by chemically binding hydrogen to a liquid carrier [12]. Finally, borohydrides and complex hydrides offer significantly higher gravimetric hydrogen storage capacities [13]. Furthermore, solid-state hydrogen storage in metal hydrides offers a promising option for developing new hydrogen storage technologies due to its advantages over conventional methods, such as high volumetric capacity and low pressure and temperature operating conditions [4,14,15].

To be considered a promising hydride, a material must have fast hydrogen intake and outtake, with high reversible capacity under mild operational conditions [16]. A promising candidate for solid-state hydrogen storage is the TiFe alloy, known for its low cost and favorable operating conditions, typically at temperatures between 30 and 70 °C, and low pressures (1–2 MPa) [17]. Despite these advantages, the TiFe alloy exhibits slow kinetics during the initial hydrogenation process (activation), primarily due to the formation of a surface oxide layer that acts as a barrier for hydrogen absorption. To address this issue, high pressure and temperature conditions are often required during activation.

To overcome this drawback, several approaches have been studied, including microstructural refinement achieved by ball milling [16,18], high-pressure torsion [19], and cold rolling [20,21]. Similarly, another important alternative involves partial element substitution of Fe and/or Ti with transition metals such as Zr [22–24], V [25], Mn [23,26], Ni [27], and Cr [28]. In most cases, transition metals have improved the kinetics by reducing or eliminating incubation time and increasing the rate at which the maximum capacity is reached.

A recent study by Peng demonstrated that the addition of ZrV₂ to TiFe alloys significantly enhances their hydrogenation properties. In particular, the TiFe + 12 wt.% ZrV₂ alloy (hereinafter referred to as the parent alloy) achieved a maximum hydrogen storage capacity of approximately 1.6 wt.% with improved first hydrogenation kinetics [29]. This parent alloy is a multiphase system, with a primary phase of TiFe-type structure, of composition Fe₃₇Ti₄₄Zr₉V₁₀, and a secondary Fe₂Ti-type phase with composition Fe₅₂Ti₄₀Zr₃V₅. It is believed that the enhancement of the first hydrogenation kinetics is associated with the secondary phase fraction, as it acts as a gateway for the hydrogen in this system. However, it is also noted that an increase in the secondary phase fraction can adversely affect the reversibility of hydrogen in the alloy. Therefore, further studies on the relationship between phase structures are necessary to understand how each phase influences hydrogen absorption and desorption capacity, the activation process, and the reaction kinetics.

This study aims to investigate the individual contributions of the primary (Fe₃₇Ti₄₄Zr₉V₁₀) and secondary (Fe₅₂Ti₄₀Zr₃V₅) phases in the parent TiFe + 12 wt.% ZrV₂ alloy to better understand their roles in the hydrogen storage behavior. The alloys were synthesized separately using arc melting and characterized through X-ray diffraction, scanning electron microscopy, and energy-dispersive spectroscopy. The hydrogen storage capacities were measured using a custom-built Sieverts apparatus. Our findings highlight the significant influence of the synthesis method on the final crystal structure and hydrogenation properties, providing valuable insights for the development of efficient hydrogen storage materials.

2. Materials and Methods

The synthesis of all samples was carried out by arc-melting under argon atmosphere. Three grams of each alloy composition were synthesized. The raw elements Ti (99.9%), Fe (99.9%), Zr (99.5%), and V (99.7%) were purchased from Alfa Aesar® (Ward Hill, MA, USA). The pellets were turned and melted four times to ensure a homogeneous composition.

Material characterization was performed using several techniques. To study the morphology, a Hitachi VP-SEM SU1510 (Mississauga, ON, Canada) scanning electron microscope equipped with an Energy Dispersive X-ray (EDX) spectrometer was used. The relative abundance of each region was quantified from backscattered electron micrographs using the image analyzing software ImageJ[®] (version 2.0) [30]. To study the crystal structure of the samples, X-ray measurements were conducted on a D8 Focus Bruker X-ray (Madison, WI, USA) powder diffractometer with Cu K α radiation. The percentage of each phase as well as crystal structure parameters were determined by Rietveld refinement method using TOPAS software (version 6) [31].

First hydrogenation (activation) was studied using a homemade Sievert-type apparatus. One gram of each alloy composition was used for the hydrogenation measurements. To prevent the formation of oxide layers, the synthesized samples were hand-crushed under an argon atmosphere. The activation of the samples was conducted at room temperature (RT) under a hydrogen pressure of 20 bars.

3. Results and Discussion

3.1. Morphology

Figure 1 shows a backscattered electron image obtained by SEM of the as-cast Fe₅₂Ti₄₀Zr₃V₅ alloy. The structure of the alloy exhibits two distinct shades of grey: a lighter gray and a darker gray. These differences in contrast suggest variations in the chemical composition throughout the alloy. Moreover, small black regions are observed. Table 1 shows the overall chemical composition of the Fe₅₂Ti₄₀Zr₃V₅ alloy, measured by EDX and compared to the nominal composition. The measured values for the alloys are close to the nominal compositions. Table 2 presents the chemical composition of each region as measured by EDX. The relative amount of each region was calculated using imageJ analysis. The light gray contrast area has a composition close to Fe₂Ti stoichiometry which was the structure seen in the parent alloy. However, the abundance determined by imageJ is around 66%. Nonetheless, the chemical composition is much closer to a ‘true’ Fe₂Ti stoichiometry than in the parent alloy. The darker gray region shows a composition close to stoichiometric TiFe, with an abundance of around 28%, while the black region consists of Ti-rich precipitates, with a measured abundance of ~6%.

Table 1. Overall chemical composition of the Fe₅₂Ti₄₀Zr₃V₅ alloy, measured by EDX and compared to the nominal composition (uncertainty is ± 0.2 for all values).

Alloy	Region	Chemical Composition (at%)			
		Fe	Ti	Zr	V
Fe ₅₂ Ti ₄₀ Zr ₃ V ₅	Nominal value	52.0	40.0	3.0	5.0
	Measured Value	50.5	40.3	4.9	4.3

Table 2. Chemical composition of Fe₅₂Ti₄₀Zr₃V₅, in at. %, of the different regions determined by EDX analysis (uncertainty is ± 0.2 for all chemical composition values).

Alloy	Region	Phase Abundance (%)	Chemical Composition (at%)			
			Fe	Ti	Zr	V
Fe ₅₂ Ti ₄₀ Zr ₃ V ₅	Light-gray	66	59.9	32.5	2.6	5.0
	Dark-gray	28	48.8	47.1	1.1	3.1
	Black	6	1.3	93.2	5.0	0.5

The presence of other phases beside the Fe₂Ti structure in the alloy, instead of a pure Fe₂Ti-type as seen in the parent alloy, can be attributed to the synthesis method. The rapid cooling and solidification inherent to the arc-melting process used for synthesis may lead to non-uniform distribution of elements, influencing phase formation and resulting in a mixture of phases rather than a single, uniform phase. Therefore, the processing conditions,

including cooling rates and local temperature gradients within the melt, play a pivotal role in determining the final microstructure.

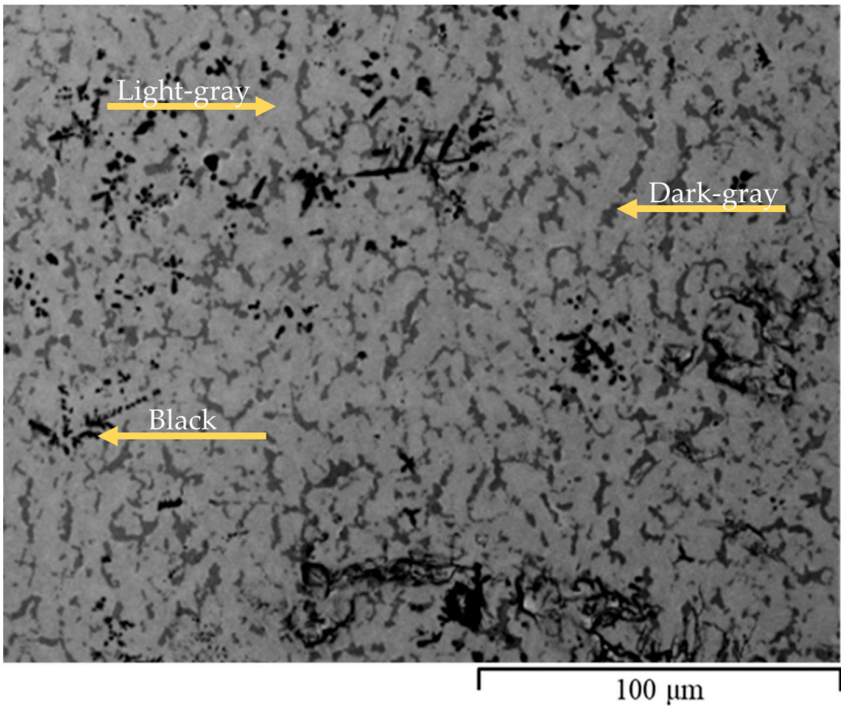


Figure 1. Backscattered electron image of Fe₅₂Ti₄₀Zr₃V₅ alloy.

Figure 2 shows a backscattered electron image obtained by SEM of the as-cast Fe₃₇Ti₄₄Zr₉V₁₀ alloy. As for the previous alloy, light and dark grey areas are present, but here the microstructure is more dendritic. Black regions are also present. Table 3 shows the overall chemical composition of the Fe₃₇Ti₄₄Zr₉V₁₀ alloy, measured by EDX and compared to the nominal composition. The measured values for the alloys are close to the nominal compositions. Table 4 presents the chemical composition of each region as measured by EDX, as well as the relative amount calculated by image analysis. Similar to the previous alloy, the black regions are Ti-rich precipitates with a measured abundance of ~4%. However, the dark gray and light gray regions show a similar composition with difference abundance, 64% and 32%, respectively. This could be an indication the dark gray and light gray regions could be the same phase, exhibiting only a slight variation in chemical composition.

Table 3. Overall chemical composition of the Fe₃₇Ti₄₄Zr₉V₁₀ alloy, measured by EDX and compared to the nominal composition (uncertainty is ±0.2 for all values).

Alloy	Region	Chemical Composition (at%)			
		Fe	Ti	Zr	V
Fe ₃₇ Ti ₄₄ Zr ₉ V ₁₀	Nominal value	37.0	44.0	9.0	10.0
	Measured Value	35.2	43.3	11.9	9.6

Table 4. Chemical composition of Fe₃₇Ti₄₄Zr₉V₁₀ alloy, in at. %, of the different regions determined by EDX analysis (uncertainty is ±0.2 for all values).

Alloy	Region	Phase Abundance (%)	Chemical Composition (at%)			
			Fe	Ti	Zr	V
Fe ₃₇ Ti ₄₄ Zr ₉ V ₁₀	Light grey	64	35.1	46.0	8.2	10.6
	Dark grey	32	37.0	40.2	12.3	10.5
	Black	4	5.3	82.4	10.3	2.1

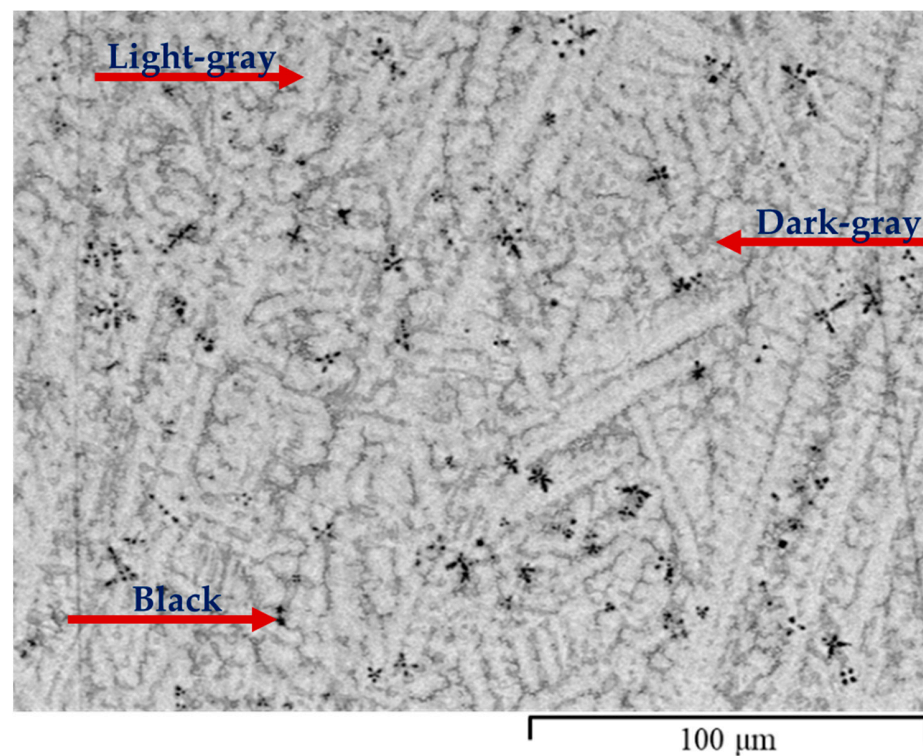


Figure 2. Backscattered electron image of $\text{Fe}_{37}\text{Ti}_{44}\text{Zr}_9\text{V}_{10}$ alloy.

3.2. Crystal Structure of As-Cast Alloys

Figure 3 shows the XRD patterns of the two studied alloys in the as-cast condition. The alloy with composition $\text{Fe}_{52}\text{Ti}_{40}\text{Zr}_3\text{V}_5$ exhibited a distinct two-phase structure, consisting of Fe_2Ti -type and TiFe phases, along with an additional notable Ti peak. Correlating with the EDX analysis in Table 2, the light grey region corresponded to the Fe_2Ti -type phase, while the dark grey region corresponded to the TiFe phase. The titanium peak identified in the XRD analysis is attributed to the presence of Ti -precipitates within the alloy. The Fe_2Ti -type phase has a hexagonal crystal structure, with space group 194 ($P6_3/\text{mmc}$), structure type MgZn_2 . The TiFe phase is characterized by a cubic crystal structure, with the space group 221 ($\text{Pm}-3\text{m}$), structure type CsCl . The Ti -precipitates also display a hexagonal crystal structure with space group 194 ($P6_3/\text{mmc}$) and structure type Mg . Table 5 shows the crystallographic parameters as determined by Rietveld refinement. First, the phase abundances agree well with the results of the ImageJ analysis of the backscattered images. Second, the lattice parameters of the individual phases are close to the literature values. The three phases are nanocrystalline. The microstrain was not refined for the Ti phase because the abundance is too low to have significant peaks at high angles. To respect the A_2B stoichiometry of the Fe_2Ti phase, Fe and V were assigned to the A site, while Zr and Ti were assigned to the B site.

Table 5. Crystallographic parameters of the as-cast samples. The number in parentheses indicates the uncertainty in the last significant digit.

Alloy	Phase	Phase Abundance (%)	a (Å)	c (Å)	Crystallite Size (nm)	Microstrain (%)
$\text{Fe}_{52}\text{Ti}_{40}\text{Zr}_3\text{V}_5$	Fe_2Ti	71.9 (4)	4.8919 (4)	7.9528 (8)	65 (6)	0.195 (3)
	TiFe	26.0 (4)	2.9835 (2)	--	34 (2)	0.077 (5)
	Ti	2.1 (2)	2.874 (1)	4.539 (4)	25 (5)	--
$\text{Fe}_{37}\text{Ti}_{44}\text{Zr}_9\text{V}_{10}$	C14	92.0 (2)	5.0109 (4)	8.1420 (9)	57 (4)	0.231 (3)
	BCC	8.0 (2)	3.1502 (4)	--	21 (1)	--

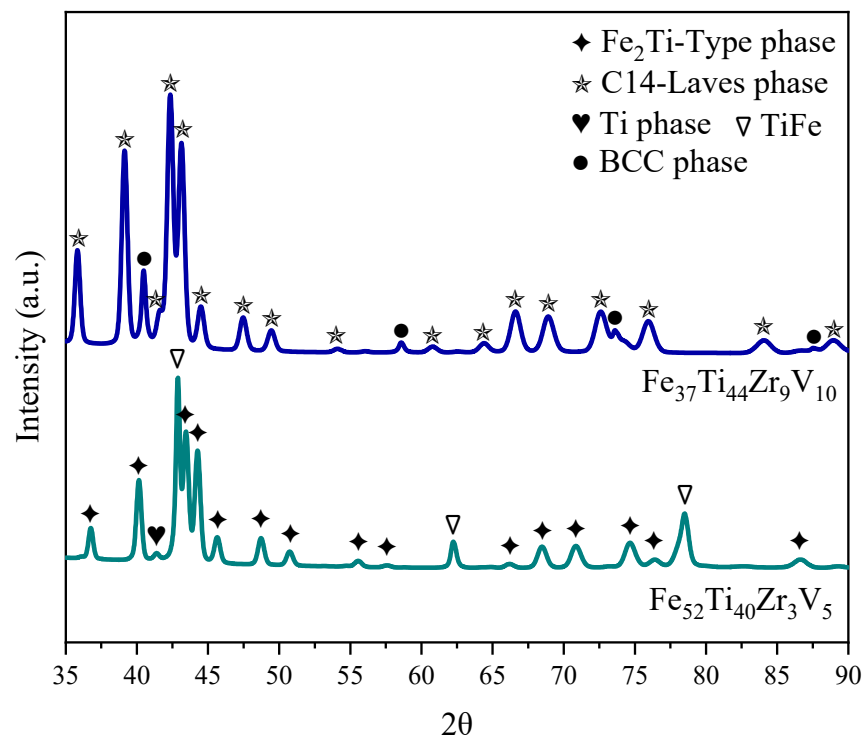


Figure 3. X-ray diffraction patterns of as-cast samples.

For the $\text{Fe}_{37}\text{Ti}_{44}\text{Zr}_9\text{V}_{10}$ alloy, a distinct two-phase system was identified: a C14-Laves phase and a cubic phase. Surprisingly, the TiFe phase was not present in this alloy, while it was the main phase in the parent alloy. This indicates that casting by arc melting under our experimental conditions results in highly metastable alloys. Table 5 shows the phase abundance and crystallographic parameters evaluated from Rietveld refinement. Considering the stoichiometry of each region seen in Figure 2, we assigned the light and dark grey regions to the C14-Laves phase and the cubic phase to the black region. Regarding the C14 phase, EDX measurements indicate an average composition of 36% Fe, 43% Ti, 10% Zr, and 11% V. To maintain the AB_2 stoichiometry, each site should accommodate more than one element. Typically, in a Laves phase, elements such as Ti and Zr are expected to occupy the A sites, while Fe and V fill the B sites [32]. However, in this case, Ti atoms should occupy both the A and B sites, a situation reported in studies of similar multicomponent systems, such as TiVFeZr [1], Zr-Ti-Ni [33], and Ti-Ni-Al [34] alloys. Based on the average composition, we assumed the A site to be 70% Ti and 30% Zr, while the B site is 54% Fe, 16% V and 30% Ti.

The second phase identified in this alloy has the composition 82% Ti, 10% Zr, 2% V, and 5% Fe. In a Zr-Ti-P investigation, Oliynyk et al. found a high-temperature phase with a composition of 89% Ti, and 11% Zr, characterized as a BCC phase, space group Im-3m , structure type W [35]. The lattice parameter in our case is smaller than the reported by Oliynyk et al., likely due to the partial replacement of Ti and Zr atoms by smaller V and Fe atoms.

3.3. First Hydrogenation (Activation)

Figure 4 shows the activation curve of both alloys. The $\text{Fe}_{52}\text{Ti}_{40}\text{Zr}_3\text{V}_5$ alloy absorbed 0.9 wt.% H_2 , while the $\text{Fe}_{37}\text{Ti}_{44}\text{Zr}_9\text{V}_{10}$ alloy demonstrated a significantly higher capacity, reaching 2.3 wt.% H_2 . In his investigation, Lv reported a capacity of 1.65 wt.%. Considering that the parent alloy was 57 wt.% $\text{Fe}_{52}\text{Ti}_{40}\text{Zr}_3\text{V}_5$ and 43 wt.% of $\text{Fe}_{37}\text{Ti}_{44}\text{Zr}_9\text{V}_{10}$, and using the capacities found in our investigation, we calculated a capacity of 1.5 wt.%. This is reasonably close to the capacity measured by Lv, considering that, in our case, the alloys were not pure Fe_2Ti and TiFe. The incubation time of the $\text{Fe}_{52}\text{Ti}_{40}\text{Zr}_3\text{V}_5$ alloy is about

the same as the parent alloy, supporting Peng's explanation that the Fe₂Ti phase acts as a gateway for hydrogen to reach the TiFe phase. As the Fe₃₇Ti₄₄Zr₉V₁₀ alloy is mainly C14 phase, which was not present in the parent alloy, we could not compare its incubation time, but it suggests that the C14 phase may be a better gateway phase than the Fe₂Ti phase.

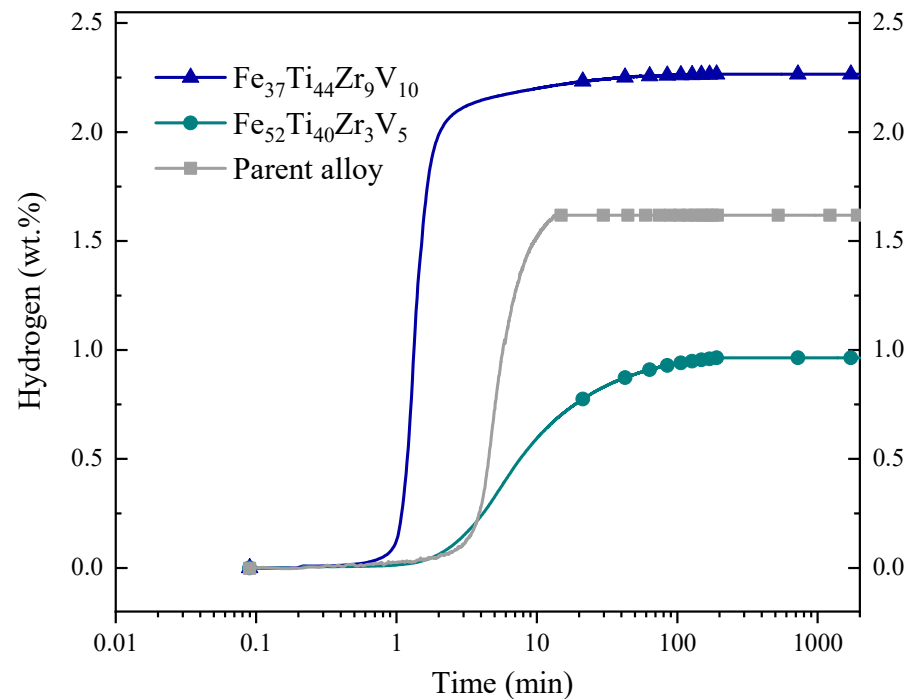


Figure 4. Activation of Fe₅₂Ti₄₀Zr₃V₅, Fe₃₇Ti₄₄Zr₉V₁₀ and TiFe + 12 ZrV₂ alloys at RT and 20 bars of hydrogen pressure.

3.4. Crystal Structure of Hydrided Alloys

Figure 5 shows the XRD patterns of the hydrogenated alloys at room temperature, while Table 6 presents their crystallographic parameters. For the Fe₅₂Ti₄₀Zr₃V₅ alloy, the XRD analysis reveals that the abundance of Fe₂Ti-type phase is essentially the same as in the as-cast alloy. The unit cell volume of this phase is slightly larger than in the as-cast state, indicating that some hydrogen is still in solid solution. Assuming a change of volume of 2.7 Å³ per hydrogen atom, we calculated that 0.3 wt.% of hydrogen is in solid solution in the Fe₂Ti-type phase. The pattern shows the presence of TiFe and TiFeH₂ peaks. The total abundance of these two phases is 23.6 wt.%, which is in good agreement with the 26 wt.% abundance of TiFe in the as-cast pattern. As the diffraction pattern was taken at room temperature in air, it is normal that the hydride phase spontaneously desorbed under these conditions. Considering that the TiFe phase fully absorbed hydrogen with a nominal capacity of 1.86 wt.%, we get a contribution of 0.48 wt.% from the TiFe phase. This, added to the estimated 0.3 wt.% from the Fe₂Ti-type phase, gives a total capacity of 0.78 wt.%, which is quite close to the measured capacity of 0.9 wt.%.

For the Fe₃₇Ti₄₄Zr₉V₁₀ alloy, the pattern consists of two phases: C14 and FCC (Face Centered Cubic). It is well known that the fully hydride form of a BCC alloy has the FCC structure. The abundance of the C14 and FCC phases perfectly matches the abundances of C14 and BCC in the as-cast state. The lattice parameters of the C14 phase are larger than those in the as-cast state, indicating that this phase is still in hydride state during the X-ray diffraction experiment.

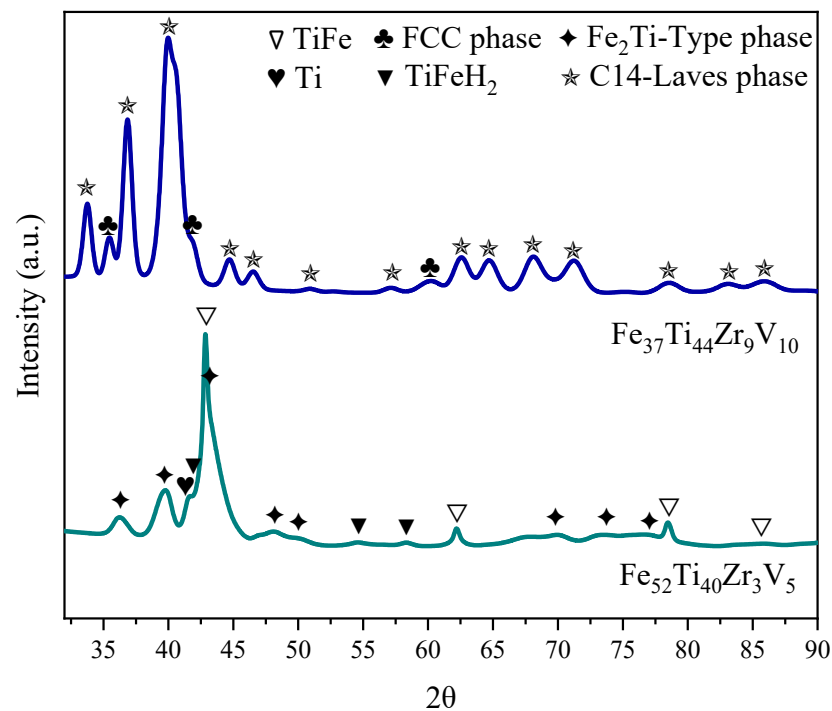


Figure 5. X-ray diffraction patterns of hydrogenated samples.

Table 6. Crystallographic parameters of the hydrogenated samples. The number in parentheses is the uncertainty on the last significant digit. For the TiFeH_2 phase, the b (Å) is 2.977 (2), and the Beta angle is 95.27° (4).

Alloy	Phase	Phase Abundance (%)	a (Å)	c (Å)	Crystallite Size (nm)	Microstrain (%)
$\text{Fe}_{52}\text{Ti}_{40}\text{Zr}_3\text{V}_5$	Fe_2Ti	69.0 (6)	4.955 (1)	8.070 (3)	45 (10)	0.75 (1)
	TiFe	15.6 (4)	2.9901 (5)	--	16.1 (5)	--
	TiFeH_2	8.2 (4)	4.738 (2)	4.670 (2)	17 (1)	--
	Ti	7.2 (4)	2.921 (2)	4.391 (5)	8.7 (6)	--
$\text{Fe}_{37}\text{Ti}_{44}\text{Zr}_9\text{V}_{10}$	C14	92.2 (3)	5.2886 (8)	8.600 (1)	29 (1)	0.443 (3)
	FCC	7.8 (3)	4.3706 (8)	--	8.8 (3)	--

4. Conclusions

This study investigated the first hydrogenation properties, microstructure, and crystal structure of the individual phases present in the parent alloy $\text{TiFe} + 12 \text{ wt.}\% \text{ ZrV}_2$. Specifically, we analyzed the $\text{Fe}_{52}\text{Ti}_{40}\text{Zr}_3\text{V}_5$ and $\text{Fe}_{37}\text{Ti}_{44}\text{Zr}_9\text{V}_{10}$ alloys. Our findings provide valuable insights into the behavior and characteristics of these phases when synthesized separately.

Both synthesized alloys exhibited distinct phases. The $\text{Fe}_{52}\text{Ti}_{40}\text{Zr}_3\text{V}_5$ alloy, expected to be a single-phase Fe_2Ti -type, exhibited a multiphase structure comprising 71.9 wt.% Fe_2Ti -type phase, 26.0 wt.% TiFe phase, and 2.1 wt.% Ti-precipitates. This indicates that our casting conditions result in the formation of metastable phases rather than a uniform single phase. Similarly, the $\text{Fe}_{37}\text{Ti}_{44}\text{Zr}_9\text{V}_{10}$ alloy, anticipated to be a TiFe-type phase, instead consisted of a 92 wt.% C14 Laves phase and an 8 wt.% BCC phase. These results highlight the critical role of synthesis methods in determining the final phase composition and microstructure of multi-element alloys.

The hydrogen storage capacity of the $\text{Fe}_{52}\text{Ti}_{40}\text{Zr}_3\text{V}_5$ alloy was limited to 0.9 wt.% due to the low hydrogen absorption by the Fe_2Ti -type phase. In contrast, the $\text{Fe}_{37}\text{Ti}_{44}\text{Zr}_9\text{V}_{10}$ alloy demonstrated a higher hydrogen storage capacity of 2.3 wt.%, attributable to the pre-

dominant C14 Laves phase. These findings emphasize the influence of phase composition on hydrogen storage performance.

The presence of multiple phases in both alloys suggests that the rapid cooling and solidification inherent to the arc-melting process induce metastability. The formation of these metastable phases under our synthesis conditions underscores the importance of controlling processing parameters, such as cooling rates and local temperature gradients, to achieve desired phase stability and optimize hydrogen storage properties.

The study illustrates that the final crystal structure and hydrogen storage properties of multi-element alloys are highly dependent on the synthesis method. Understanding the relationship between processing conditions and phase formation is crucial for designing efficient hydrogen storage materials. Further research is needed to explore alternative synthesis techniques that can stabilize desired phases and enhance hydrogen storage capacities.

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