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Study of the Microstructural and First Hydrogenation Properties of TiFe Alloy with Zr, Mn and V as Additives

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Abstract: In this paper, we report the effect of adding Zr + V or Zr + V + Mn to TiFe alloy on microstructure and hydrogen storage properties. The addition of only V was not enough to produce a minimum amount of secondary phase and, therefore, the first hydrogenation at room temperature under a hydrogen pressure of 20 bars was impossible. When 2 wt.% Zr + 2 wt.% V or 2 wt.% Zr + 2 wt.% V + 2 wt.% Mn is added to TiFe, the alloy shows a finely distributed Ti₂Fe-like secondary phase. These alloys presented a fast first hydrogenation and a high capacity. The rate-limiting step was found to be 3D growth, diffusion controlled with decreasing interface velocity. This is consistent with the hypothesis that the fast reaction is likely to be the presence of Ti₂Fe-like secondary phases that act as a gateway for hydrogen.

Keywords: TiFe alloy; first hydrogenation kinetics; hydrogen storage

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1. Introduction

Hydrogen storage in metal hydrides is a promising way to store hydrogen [1]. In particular, TiFe alloy is a good candidate for stationary applications due to its reasonable gravimetric hydrogen capacity (~1.9 wt.%), low cost, and acceptable working temperature and pressure [2,3]. Hydrogenation of TiFe hydride is the succession of first formation of α -solid solution TiFeH_{0.1} followed by the TiFeH₁ monohydride (β) and dihydride TiFeH₂ (γ). The effect of gaseous impurities such as O₂, H₂O, CO₂ and CO on the hydrogenation kinetics of TiFe alloy was studied by Sandrock et al., which resulted in a decrease in the reaction rate and reduced hydrogen capacity [4]. These kinds of gaseous impurities hinder the dissociation of hydrogen molecules during the chemisorption step. Additionally, the formation of a surface oxide layer during the synthesis of TiFe or handling in the air makes the first hydrogenation difficult. Therefore, before the first hydrogenation, the alloy usually needs to be prepared by submitting it to high temperature and hydrogen pressure. This step is required to break the surface oxide [3]. To replace this step, mechanical treatments such as severe plastic deformation techniques [5,6] and ball milling [7–12] have been investigated. Mechanical treatment creates new surfaces and cracks for hydrogen diffusion, which facilitate the first hydrogenation. A partial substitution or addition of transition metals such as Zr [13–15], V [16], Mn [17,18], Cu [19], and Co [20] to the TiFe alloy is

also an alternative method for enhancing the first hydrogenation kinetics and flattening the plateau region in the pressure composition isotherm (P-C-T). Recently, it has been shown that simultaneous addition of Zr and Mn could enhance the first hydrogenation kinetics [21]. This improvement was explained by the existence of a Ti_2Fe -type secondary phase, which acts as a gateway for hydrogen to reach the main TiFe phase [22]. The actual composition of the Ti_2Fe -type phase is found to be $(\text{Ti,Zr,Mn})_2\text{Fe}$ by the chemical composition analysis, where Zr and Mn substitute for Ti [21]. However, in the phase equilibrium diagram of Ti-Fe, only TiFe and TiFe_2 are seen [23]. A Ti_2Fe metastable phase was identified by Dong et al. [24]. It was also seen in the Ti-Fe-B system [25] and Ti-Fe-Zr ternary alloys [26].

Earlier studies in the literature mentioned that partial substitution of iron by vanadium is beneficial for enhancing the first hydrogenation [16]. It is also known from previous reports that the addition of Zr is effective but a certain level (4 wt.%) of zirconium is essential [15,21]. In this paper, the addition of Zr along with V and Mn is reported. The goal of this investigation was to lower the concentration level of Zr. TiFe alloys with only V (at a concentration level of 2, 4 wt.%) were also studied in order to know the effect of individual elements on the first hydrogenation of TiFe alloy. It is known from previous investigations that the most effective combination in terms of kinetics and maximum hydrogen capacity is a TiFe alloy with simultaneous addition of 2 wt.% Mn and 4 wt.% Zr [21]. In this paper, we also report on the simultaneous addition of 2 wt.% Zr + 2 wt.% Mn + 2 wt.% V to TiFe alloy. This combination was chosen to investigate a possible synergetic effect when many elements are added at a low concentration level.

2. Materials and Methods

TiFe alloys with V (2 and 4 wt.%), a combination of 2 wt.% Zr + 2 wt.% V, and a combination of 2 wt.% Zr + 2 wt.% Mn + 2 wt.% V were synthesized by GKN Sinter Metals Engineering GmbH, Dahlienstraße 43, D-42477 Radevormwald, Germany using induction melting of melt size ~6.5 kg. Industrial-grade Fe (ASTM 1005) and Ti (ASTM B265 grade 1) with Ferrovandium (80.09 wt.% V, 18.75 wt.% Fe, 0.85 wt.% Al, 0.04 wt.% P, 0.23 wt.% C, and 0.04 wt.% S) and electrolytic manganese (99.7 wt.%) were used as raw materials. The bulk composition of these alloys was measured by an X-ray fluorescence spectrometer (Bruker XRF S1titan) and a comparison of nominal values with the XRF measurements is shown in Table 1. Please note that in this table, the element's abundances are in at.%. It could be seen that bulk composition is close to the nominal one. However, for the alloy with 2 wt.% Zr + 2 wt.% V and the alloy with 2 wt.% Zr + 2 wt.% Mn + 2 wt.% V, the alloys are titanium-rich and vanadium-depleted compared to the nominal values.

Table 1. Measured bulk composition analysis by XRF (X-ray fluorescence) spectrometer of all alloys with nominal values. Uncertainty on all values is ± 1 at.%.

Alloy		Ti (at.%)	Fe (at.%)	Zr (at.%)	V (at.%)	Mn (at.%)
TiFe+ 2 wt.% V	Nominal composition	49	49		2	
	Measurement	49	48		2	
TiFe+ 4 wt.% V	Nominal composition	48	48		4	
	Measurement	49	47		4	
TiFe+ 2 wt.% Zr + 2 wt.% V	Nominal composition	48	48	1	2	
	Measurement	54	43	1	2	
TiFe+ 2 wt.% Zr + 2 wt.% Mn + 2 wt.% V	Nominal composition	48	47	1	2	2
	Measurement	53	41	1	2	2

The prepared ingots were crushed in air to obtain small chunks for characterization. These small chunks were thereafter hand crushed in an argon atmosphere using a hardened steel mortar and pestle. For hydrogen absorption measurements, 1 g of powder was filled in a sample holder under an argon atmosphere. First hydrogenation kinetics were obtained

using a homemade Sievert-type apparatus. The hydrogenation tests were performed at room temperature under 20 bars of hydrogen pressure. The first hydrogenation was performed without any prior heat treatment or extended degassing. Back-scattered micrographs and the chemical composition of different phases were acquired using a Hitachi SU-3500 scanning electron microscope (SEM) equipped with an EDX (Energy Dispersive X-ray) spectrometer from Oxford Instruments. Three consecutive measurements were taken for the determination of uncertainty values. X-ray diffraction patterns were obtained using a Bruker D8 Focus diffractometer with Cu α radiation. Rietveld refinement of each X-ray pattern was performed using Topas software [27].

3. Results and Discussions

3.1. Morphology

Back-scattered electron micrographs of TiFe alloy with different additive combinations are shown in Figure 1. The micrograph of these alloys shows a grey phase (TiFe) and secondary phases (light grey, bright, dark grey). Samples with only vanadium as an additive produced a small amount of secondary phase. The addition of 2 wt.% Zr + 2 wt.% V produced a very fine distribution of the secondary phase. When 2 wt.% Zr + 2 wt.% V + 2 wt.% Mn was added to TiFe alloy, there was no significant change in the amount of secondary phase compared to the alloy with 2 wt.% Zr + 2 wt.% V.

Figure 1. Back-scattered electron micrograph of TiFe alloy with (a) 2 wt.% V; (b) 4 wt.% V; (c) 2 wt.% Zr + 2 wt.% V; (d) 2 wt.% Zr + 2 wt.% V + 2 wt.% Mn as additives.

EDX analyses of TiFe alloys with V as an additive are shown in Figure 2. It should be pointed out that these images are not representative of the abundance of the individual phases. These areas were selected for the analysis of the chemical compositions of the phases and not for an estimation of phase abundance. The chemical composition of each phase is shown in Table 2. In both alloys, three phases are present: (1) grey phase, (2) dark grey phase, and (3) light grey phase. The grey phase is TiFe with some vanadium. In both alloys, the light grey phase has an almost Ti_2Fe stoichiometry. In fact, it seems that vanadium substitutes for titanium, and the actual composition is $(\text{Ti},\text{V})_2\text{Fe}$. The dark grey phase is Ti-rich. In the case of 4 wt.% V, there is one bright phase, which has a composition close to TiFe_2 .

Figure 2. EDX analysis of TiFe with the addition of V only (a) 2 wt.% V; (b) 4 wt.% V.

Table 2. Chemical composition of each phase present in alloys with V only (uncertainty on all values is ± 1).

Alloys	Ti (at.%)	Fe (at.%)	V (at.%)
TiFe + 2 wt.% V			
Area 1 (grey phase)	49	48	3
Area 2 (light grey phase)	61	34	6
Area 3 (dark grey phase)	72	21	7
TiFe + 4 wt.% V			
Area 1 (grey phase)	48	49	4
Area 2 (light grey phase)	58	34	8
Area 3 (dark grey phase)	67	22	11
Area 4 (bright phase, TiFe_2)	38	56	6

The micrograph of the alloy with the addition of 2 wt.% Zr + 2 wt.% V is shown in Figure 3. Here, four different regions could be identified: (1) grey phase, (2) light grey phase, (3) bright phase and (4) dark grey phase. The chemical composition of each phase is listed in Table 3. The grey phase has the composition of TiFe with ~ 2 at.% of V, but Zr is absent in this phase. As for the preceding system, the light grey phase seems to have a Ti_2Fe -type composition, but here, vanadium and zirconium seem to substitute for titanium, giving a $(\text{Ti,V,Zr})_2\text{Fe}$ composition. The bright phase is the phase with the highest proportion of zirconium. It should be noted that this phase is at the edge between the grey phase and light grey phase. Moreover, the composition is close to the light grey phase except for the higher proportion of Zr. The dark grey phase is Ti-rich. The average grain size of each phase was calculated by Image J software using the 100 μm scale back-scattered micrograph [28]. For 2 wt% V, the estimated average grain size of the TiFe phase is $71 \pm 1 \mu\text{m}$. For the secondary Ti_2Fe -type and Ti-rich phases, the average grain sizes are, respectively, $11 \pm 1 \mu\text{m}$ and $12 \pm 1 \mu\text{m}$. In the case of the 4 wt% V, the average grain sizes of TiFe, Ti_2Fe -type, Ti and TiFe_2 phases are, respectively, $72 \pm 2 \mu\text{m}$, $7 \pm 1 \mu\text{m}$, $8 \pm 1 \mu\text{m}$ and $36 \pm 1 \mu\text{m}$.

Figure 3. EDX analysis of TiFe with the simultaneous addition of 2 wt.% Zr + 2 wt.% V.

Table 3. Chemical composition of each phase present in TiFe with the simultaneous addition of 2 wt.% Zr + 2 wt.% V (uncertainty on all values is ± 1).

Alloy	Ti (at.%)	Fe (at.%)	V (at.%)	Zr (at.%)
TiFe + 2 wt.% Zr + 2 wt.% V				
Area 1 (grey phase)	50	48	2	
Area 2 (light grey phase)	61	33	4	3
Area 3 (bright phase)	54	29	4	14
Area 4 (dark grey phase)	72	22	5	2

Figure 4 shows a micrograph of the TiFe alloy with the addition of 2 wt.% Zr + 2 wt.% V + 2 wt.% Mn. The chemical composition of each phase is given in Table 4. The grey phase is TiFe with about 2 at.% of Mn and V. It seems that both Mn and V substitute for iron. Zr is seen only in trace amount in this phase. As seen in the preceding system, the bright phase is at the edge of the light grey phase. The light grey phase could be written as $(\text{Ti,V,Zr,Mn})_2\text{Fe}$ with a proportion of Zr higher than for the light grey phase when V and Zr are added to TiFe. The bright phase is, again, the phase that has the highest proportion of zirconium, and the chemical composition is close to the bright phase as seen for TiFe + 2 wt.% Zr + 2 wt.% V. Dark grey is Ti-rich, as was seen for the other additions. The average grain sizes of TiFe, Ti_2Fe -type (light), Ti_2Fe -type (bright) and Ti phases for alloy with 2 wt.% Zr + 2 wt.% V are, respectively, $88 \pm 1 \mu\text{m}$, $23 \pm 1 \mu\text{m}$, $11 \pm 1 \mu\text{m}$ and $22 \pm 1 \mu\text{m}$. In the case of 2 wt.% Zr + 2 wt.% V + 2 wt.% Mn, the average grain sizes were: $77 \pm 1 \mu\text{m}$ for TiFe, $14 \pm 1 \mu\text{m}$ for Ti_2Fe -type (light), $8 \pm 1 \mu\text{m}$ for Ti_2Fe -type (bright), and $18 \pm 1 \mu\text{m}$ for Ti.

Figure 4. EDX analysis of TiFe alloy with the simultaneous addition of 2 wt.% Zr + 2 wt.% V + 2 wt.% Mn.

Table 4. Chemical composition of TiFe + 2 wt.% Zr + 2 wt.% V + 2 wt.% Mn (uncertainty on all values is ± 1).

Alloy	Ti (at.%)	Fe (at.%)	V (at.%)	Zr (at.%)	Mn (at.%)
TiFe + 2 wt.% Zr + 2 wt.% V + 2 wt.% Mn					
Area 1 (grey phase)	50	47	2	<1	2
Area 2 (light grey phase)	57	32	3	7	2
Area 3 (bright phase)	45	33	5	14	3
Area 4 (dark grey phase)	78	17	5	3	2

3.2. Crystal Structure

The X-ray diffraction (XRD) pattern of each alloy is shown in Figure 5. The X-ray pattern of TiFe without additive is shown as a reference where the presence of TiFe phase with TiFe_2 phase could be seen [21]. For all patterns, the main phase is TiFe (space group Pm-3m), which corresponds to the matrix seen in the SEM micrographs. All patterns of alloys with additives also show a small peak at around $2\theta = 45^\circ$. This peak could be assigned to the Ti_2Fe -like phase (space group Fd-3m) that was identified from the EDX investigation. The Ti_2Fe phase used in the Rietveld refinement was given the chemical composition of the light grey phase indicated in Table 2, with vanadium occupying the same site as titanium. The other phases seen in Figure 2 have too small of an abundance to be seen on the diffraction pattern.

Regarding the pattern of TiFe with 2 wt.% Zr + 2 wt.% V addition, beside the TiFe and Ti_2Fe peaks, we see the appearance of new Bragg peaks around 40° . Again, using the EDX results shown in Table 3, we could assign some peaks to a Ti phase, which corresponds to the dark grey phase. The remaining peaks could be indexed to a second Ti_2Fe phase but with larger lattice parameters than the light grey Ti_2Fe phase seen in all patterns. The reason why there are two Ti_2Fe -like phases with different lattice parameters could be the following. The light grey phase seen on all micrographs has a similar chemical composition with Fe on one site and the other elements substituting the titanium on the other sites. The micrographs and EDX analysis show that the bright phase in the TiFe + 2 wt.% Zr + 2 wt.% V alloy is at the edge of the light grey phase and has a much larger proportion of zirconium. The EDX results show that zirconium seems to substitute for titanium. As zirconium has a bigger atomic radius than titanium (1.6 Å for Zr and 1.47 Å for Ti), it could be expected that the lattice parameters will also be bigger. Therefore, the explanation of the two Ti_2Fe -like phases is that during cooling, the Ti_2Fe -like phase is split into two compositions: one with low zirconium content and the other, at the edge, with high zirconium content. They will be respectively identified as $(\text{Ti}, \text{V}, \text{Zr})_2\text{Fe}$ and $(\text{Ti},$

V, Zr)₂Fe-Zr-rich. The same phenomenon is seen for the TiFe + 2 wt.% Zr + 2 wt.% V + 2 wt.% Mn alloy. The crystallographic parameters extracted from Rietveld refinements are listed in Table 5. A reference list of crystallographic parameters of TiFe without additive is also shown in Table 5 for comparison.

Figure 5. X-ray pattern of TiFe alloys with the addition of only V, Zr + V, and Zr + V + Mn. The without additive curve is reproduced with permission from Patel et al., Microstructure and first hydrogenation properties of TiFe alloy with Zr and Mn as additive; published by Elsevier, 2020.

Table 5. Refined value of phase abundance, lattice parameters, crystallite size, cell volume and microstrains by Rietveld refinement of each alloy's X-ray patterns. Error on the last significant digit is indicated in the parentheses.

Phase Name	Phase Abundance (%)	Lattice Parameter (Å)	Cell Volume (Å ³)	Crystallite Size (nm)	Microstrain (%)
TiFe without additive [21]					
TiFe	93(1)	a = 2.9773(2)	26.39(6)	31(1)	0.08(4)
TiFe ₂	7(1)	a = 4.709(2) c = 7.968(1)	153.0(2)	36(2)	—
2 wt.% V					
TiFe	90(2)	a = 2.9810(4)	26.49(1)	35(2)	0.145(3)
(Ti,V) ₂ Fe	10(2)	a = 10.533(3)	1168(1)	18(3)	—
4 wt.% V					
TiFe	91(2)	a = 2.9806(4)	26.48(1)	29(1)	0.161(4)
(Ti,V) ₂ Fe	9(1)	a = 10.532(3)	1168(1)	18(3)	—
2 wt.% Zr + 2 wt.% V					
TiFe	68(2)	a = 2.9856(3)	26.613(7)	32(1)	0.068(4)
Ti	9(1)	a = 2.991(2) c = 4.678(5)	36.25(6)	18(3)	—
(Ti,V,Zr) ₂ Fe	9(1)	a = 10.522(3)	1167.0(9)	22(4)	—
(Ti,V,Zr) ₂ Fe-Zr-rich	14(1)	a = 11.411(3)	1486(1)	17(2)	—
2 wt.% Zr + 2 wt.% V + 2 wt.% Mn					
TiFe	69(2)	a = 2.9878(3)	26.671(7)	24.8(9)	0.02(1)
Ti	6(1)	a = 2.991(2) c = 4.685(5)	36.29(6)	32(12)	—
(Ti,V,Zr,Mn) ₂ Fe	8(1)	a = 10.543(3)	1172(1)	29(7)	—
(Ti,V,Zr,Mn) ₂ Fe-Zr-rich	18(1)	a = 11.438(2)	1496.4(8)	24(3)	—

From Figure 2, and Tables 2 and 5, we see that the addition of 2 or 4 wt.% V has basically the same effect. The abundance of TiFe and secondary phase is practically constant as well as their chemical composition. The stoichiometry of the secondary phase measured by EDX agrees with the Ti_2Fe -like crystal structure seen in the diffraction patterns. Figure 2b showed a TiFe_2 -like phase but the amount of that phase was too small to be seen in the diffraction pattern. Crystallite sizes and microstrains are similar for the two compositions.

When Zr and V are added simultaneously, the proportion of secondary phases drastically increases compared to when only V is added. It indicates that Zr favors the formation of the secondary phase. Table 3 shows that, in fact, Zr is almost absent from the TiFe phase, unlike V, which seems to substitute for Fe. Beside the main TiFe phase, the diffraction pattern showed peaks belonging to Ti, and two Ti_2Fe -like crystal structures that differ by their lattice parameters. This agrees quite well with what was reported in Table 3. As discussed before, the light grey phase and the bright phase could be associated, respectively, with the $(\text{Ti,V,Zr})_2\text{Fe}$ and $(\text{Ti,V,Zr})_2\text{Fe}$ -Zr-rich phases. Simultaneous addition of V, Zr and Mn resulted in basically the same phase composition as when Zr and V are added together. The phases identified in Figure 3 are also present in the diffraction pattern.

From these results, it could be concluded that the addition of 2 wt.% Zr + 2 wt.% V and 2 wt.% Zr + 2 wt.% V + 2 wt.% Mn leads to the formation of a large proportion of the secondary phase at ~32% (by adding the phase abundance of Ti_2Fe , Ti_2Fe -Zr-rich, and Ti) compared to the alloys with only V, where it was only 10%. The lattice parameter of the major phase TiFe increases slightly with the number of additives. The Zr-rich Ti_2Fe -like phase has a larger lattice parameter than the other Ti_2Fe -like phase. The crystallite size and microstrain for all phases do not seem to depend on the nature and amount of additive.

3.3. Activation Kinetics

First hydrogenation (activation) curves of all TiFe alloys with additives are shown in Figure 6. The TiFe without additive and alloys with V addition did not absorb hydrogen, even after 20 h of hydrogen exposition. The reason could be the small proportion of Ti_2Fe -like phase ~10%, as quantified by X-ray diffraction pattern analysis.

Figure 6. Activation kinetics of TiFe alloy with V, Zr + V and Zr + V + Mn under 20 bar H_2 pressure at room temperature. The without additive curve is reproduced with permission from Patel et al., Microstructure and first hydrogenation properties of TiFe alloy with Zr and Mn as additive; published by Elsevier, 2020.

The combination of 2 wt.% Zr + 2 wt.% V leads to good kinetics and reaches its maximum hydrogen capacity (1.7 wt.%) in 6 h. Previously, it has been shown that alloy with 2 wt.% Zr does not activate, while TiFe with 4 wt.% Zr attained a capacity of 1.2 wt.% hydrogen after 20 h [21]. Therefore, it seems that having both Zr and V as additives is a better strategy to improve activation than just increasing the amount of Zr. TiFe alloy with the simultaneous addition of 2 wt.% Zr + 2 wt.% V + 2 wt.% Mn has a slightly higher hydrogen capacity (1.8 wt.%) than the alloy with 2 wt.% Zr + 2 wt.% V (1.7 wt.%). As both alloys have less than 70% TiFe phase, the measured capacity is not only due to absorption by the TiFe phase. Considering that all phases form a dihydride, the maximum theoretical hydrogen capacity of the TiFe, Ti, and Ti₂Fe phases are, respectively, 1.9 wt.%, 4 wt.%, and 1.3 wt.%. Using the phase abundance given by Rietveld refinement, a total capacity of 1.9 wt.% is found for the alloy with 2 wt.% Zr + 2 wt.% V + 2 wt.% Mn addition. This agrees with the measured capacity. However, similar calculation for the alloy with 2 wt.% Zr + 2 wt.% V addition gives a capacity of 1.95 wt.%, which is much higher than the measured capacity. Therefore, the hydrogen absorption of individual phases is not well determined at this moment.

3.4. Rate-Limiting Step of First Hydrogenation

In order to understand the activation mechanism of the alloys with additive, the rate-limiting step was determined. Table 6 shows the most typical models and their mathematical expressions. In these equations, α represents the transformed ratio, i.e., the ratio of absorbed hydrogen quantity divided by the maximum hydrogen capacity. Other parameters are the rate constant (k) and the time (t). Plotting the left side of the model equations as a function of t should give a linear curve for the correct model of rate-limiting step.

Table 6. Model equations for rate limiting step determination.

Rate Limiting Step Model Name	Model Equation	Description
Chemisorption	$\alpha = kt$	Surface controlled [29]
Nucleation-growth-impingement model (JMA2D)	$[-\ln(1 - \alpha)]^{1/2} = kt$	2D growth of existing nuclei with constant velocity [29,30]
Nucleation-growth-impingement model (JMA3D)	$[-\ln(1 - \alpha)]^{1/3} = kt$	3D growth of existing nuclei with constant velocity [29,30]
Contracting volume (CV2D)	$1 - (1 - \alpha)^{1/2} = kt$	2D growth with constant interface velocity [29]
Contracting volume (CV3D)	$1 - (1 - \alpha)^{1/3} = kt$	3D growth with constant interface velocity [29]
Ginstling–Brounstein model (GB2D)	$(1 - \alpha) \ln(1 - \alpha) + \alpha = kt$	2D growth, diffusion controlled with decreasing interface velocity [31]
Ginstling–Brounstein model (GB3D)	$1 - (2\alpha/3) - (1 - \alpha)^{2/3} = kt$	3D growth, diffusion controlled with decreasing interface velocity [29]

The linear fit of the different kinetic models for the TiFe alloy with 2 wt.% Zr + 2 wt.% V and 2 wt.% Zr + 2 wt.% V + 2 wt.% Mn addition is presented in Figure 7. Table 7 shows the adjusted R^2 value for each model. The GB3D model was found to be the best model for both alloys. This conclusion is in agreement with previous studies that also found the GB3D model to be the best fit for the first hydrogenation of TiFe alloys [32,33].

Figure 7. Linear fitting of each rate limiting step model for activated alloys (a) 2wt.% Zr + 2 wt.% V; (b) 2 wt.% Zr + 2 wt.% V + 2 wt.% Mn.

Table 7. Adjusted R^2 value for the linear regression of different kinetic model.

Adjusted R^2	Chemisorption	JMA2D	JMA3D	CV2D	CV3D	GB2D	GB3D
2 wt.% Zr + 2 wt.% V	0.661	0.791	0.713	0.818	0.861	0.912	0.942
2 wt.% Zr + 2 wt.% V + 2 wt.% Mn	0.670	0.794	0.717	0.818	0.859	0.917	0.942

4. Conclusions

The microstructure and first hydrogenation properties of TiFe with the addition of V only, a combination of Zr + V and a combination of Zr + V + Mn were studied. It was found that TiFe with V addition could not be activated at room temperature. However, activation was possible with simultaneous additions of 2 wt.% Zr and 2 wt.% V. As the addition of 2 wt.% of Zr alone is ineffective, this means that there is some synergetic effect when Zr and V are simultaneously added to TiFe alloy. Simultaneous additions of 2 wt.% Zr, 2 wt.% V and 2 wt.% Mn to TiFe are also beneficial in terms of improving the kinetics and the capacity. The main reason for the fast activation of alloys with (Zr, V) and (Zr, V, Mn) addition is likely to be the presence of Ti_2Fe -like secondary phases that act as a gateway for hydrogen. The thermodynamic parameters and the effect of cycling on the hydrogen storage properties will be the subject of a future investigation.

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