First hydrogenation enhancement in TiFe alloys for hydrogen storage

Catherine Gosselin\textsuperscript{1}, Dilson Santos\textsuperscript{2} and Jacques Huot\textsuperscript{1}

\textsuperscript{1} Hydrogen Research Institute, Université du Québec à Trois-Rivières, 3351 des Forges, Trois-Rivières, QC, G9A 5H7, Canada
\textsuperscript{2} Program of Metallurgical and Materials Engineering—COPPE/Federal University of Rio de Janeiro, PO Box 68505, 21941-972 Rio de Janeiro, RJ, Brazil

E-mail: jacques.huot@uqtr.ca

Received 24 December 2015, revised 1 June 2017
Accepted for publication 4 July 2017
Published 23 August 2017

Abstract
In this paper, we report the first hydrogenation kinetics of TiFe + X wt.% Zr with X = 4, 8, 12, and 16. We found that these alloys are multiphase with a TiFe matrix having about 1 at.% of zirconium in it and two secondary phases, which are rich in zirconium but also contain Ti and Fe. When X increases, the chemical composition of one of the secondary phases stays constant but the other secondary phase presents a change of composition. The sample with X = 8 presented the fastest first hydrogenation kinetics. Hydrogen capacity increases with increasing X but for X greater than 8, there was the appearance of an incubation time. The secondary phases are probably acting as a gateway for hydrogen, thus facilitating the hydrogen absorption in the TiFe phase.

Keywords: TiFe alloy, hydrogen storage, secondary phase, zirconium

(Some figures may appear in colour only in the online journal)

1. Introduction

Metal hydrides are a class of materials that could reversibly store hydrogen in a compact way. For more than 40 years, many types of metal hydrides have been studied, but large-scale applications are still limited. This is due to a number of factors, such as too high a temperature of operation, a low gravimetric capacity, slow kinetics, cost, etc. One of the earliest metal hydrides considered for practical applications was TiFe \cite{ref1}. This alloy could store hydrogen near-room temperature (RT) and under a mild pressure environment \cite{ref2}. However, one problem that increases the cost of this hydride is its poor first hydrogenation, the so-called activation. Typically, the activation of TiFe has to be performed at high temperature and under high hydrogen pressure for a long period of time \cite{ref3}. For large-scale production, the activation should ideally be performed at room temperature and under low hydrogen pressure.

One natural way to solve the activation problem is to partially substitute Ti and/or Fe with a transition metal, such as Mn, Cr, Ni, and Zr \cite{ref4–ref8}. These partial substitutions improve the activation process by reducing the absorption time and the hydrogen pressure \cite{ref9}. However, the thermodynamics and hydrogen storage capacities are also modified. An ideal solution would be to use a technique which improves the activation process without changing the thermodynamics and capacity of TiFe. From this perspective, various methods have been investigated: pulse current-assisted reaction \cite{ref10}, ball milling \cite{ref3, ref11}, plastic deformations \cite{ref12}, and utilizing clusters \cite{ref13}.

In previous studies, we have shown that the addition of Zr\textsubscript{7}Ni\textsubscript{10} and Zr greatly enhances the activation of TiFe \cite{ref14–ref16}. It was found that zirconium is the main element responsible for the fast activation and that the microstructure consisted of a TiFe matrix with a small amount of Zr in solid solution, along with a secondary phase which was zirconium rich. It was also found that the minimum amount of zirconium required to get fast activation was 4wt.%. In fact, activation was possible on as-cast materials at room temperature and under the relatively low hydrogen pressure of 2500–4500 kPa.

In the present investigation, in order to fully understand the mechanism responsible for the fast activation in TiFe doped with Zr, we studied alloys of composition TiFe + x wt.%Zr where x = 4, 8, 12, and 16. Here, the discrepancies between the present investigation and the one by Nagai \textit{et al} \cite{ref9} should...
be pointed out. The main difference with the present work is that Nagai et al. [9] studied the alloys TiFe$_{1-y}$Zr$_y$ ($y = 0.1, 0.2,$ and 0.3) that substituted iron by zirconium, while, in the present study, zirconium is added to TiFe. It was also recently shown that adding zirconium or substituting it for iron or titanium resulted in totally different microstructures and hydrogen storage properties [17].

### 2. Experimental details

Alloys were synthesized by arc melting using commercial Fe (99.9%), Ti sponge (99.9%) and Zr sponge (99.5%), which were all purchased from Alfa Aesar and used without further purification. For each synthesis, all of the raw elements were mixed in the right proportions and melted together using an arc melting apparatus working at 240 volts (V) and 60 amperes (A). For each melting, the pellet was turned over three times and remelted to ensure homogeneity. The pellet was then hand crushed using a steel mortar and pestle under Argon atmosphere or in air. X-ray powder diffractions were registered on a Bruker Advance diffractometer using copper radiation. Rietveld refinements of the x-ray diffraction patterns were performed using Topas software [18].

The microstructure and chemical analysis of the as-cast alloys were carried out using a JEOL JSM-5000 scanning electron microscope, equipped with an Oxford EDX (Energy Dispersive X-ray) apparatus. A homemade Sieverts-type apparatus was used to measure the hydrogen storage properties of the alloys. For hydrogenation measurements, the samples were filled in a reactor cell and kept under vacuum for 1 h at room temperature, before exposing them to hydrogen. The measurements were done at room temperature (RT) under a hydrogen pressure of 2500 kPa for absorption.

### 3. Results

#### 3.1. Morphology

In order to get a better contrast, the scanning electron micrographs were registered using the backscattering radiation. Figure 1 shows the microstructure of all compositions at low magnification.

It is clear that the amount of zirconium has a strong effect on the microstructure. For 4 wt.% Zr, the alloy is made up of a main matrix (grey phase) with an evenly distributed small bright phase. There are also black precipitates. For 8 wt.% Zr, the proportion of the bright phase is higher and the black precipitate seems to be of a smaller size. The sample with 12 wt.% Zr shows an almost equal proportion of bright and grey phases. The black precipitates are also noticeable. Finally, for the highest content of zirconium (16 wt.%), there is a higher proportion of bright phases than the grey phase and the black precipitates are smaller. The composition of each alloy was verified by performing an EDX quantitative analysis on the micrograph’s whole area. The results are presented in Table 1.

| Sample | Ti  | Fe  | Zr  |
|--------|-----|-----|-----|
| $x = 4$ Nominal composition | 48.85 | 48.85 | 2.3 |
| Measured | 49.1 | 48.2 | 2.6 |
| $x = 8$ Nominal composition | 47.65 | 47.65 | 4.7 |
| Measured | 49.2 | 45.8 | 5.0 |
| $x = 12$ Nominal composition | 46.4 | 46.4 | 7.2 |
| Measured | 49.9 | 41.6 | 8.5 |
| $x = 16$ Nominal composition | 45.1 | 45.1 | 9.8 |
| Measured | 50.3 | 39.5 | 10.1 |

Figure 1. Backscattered radiation micrographs of as-cast TiFe $+ x$ wt.% Zr ($x = 4, 8, 12, 16$). All values are in at.%.
We see that for all compositions, the measured and nominal abundances of Zr agree. However, the relative abundances of iron and titanium do not match so well the nominal compositions. As will be shown below, the gray phase is TiFe, the bright phase is zirconium rich and the black precipitates are almost exclusively titanium. The most likely explanation for the discrepancies between the nominal values and measured ones in the case of Ti and Fe is the random distribution of the Ti precipitates, which could bias the element abundance.

To have a better understanding of the element distributions, a chemical mapping using EDX was performed at a higher magnification. Figure 2 shows the element mapping of the as-cast alloy TiFe\(_4\) wt.% Zr.

It is clear from figure 2 that iron is evenly distributed and that zirconium is mainly in the bright phase. Close inspection shows that titanium is slightly less abundant in the bright phase than in the grey phase. The quantitative chemical composition of each phase was evaluated by performing EDX on specific points. Table 2 shows the results for TiFe + 4 wt.% Zr.

From table 2, it is clear that the main grey phase is TiFe with a small amount of iron being substituted by zirconium. The bright phase also contains iron and titanium, but the zirconium concentration is much higher. In fact, it seems that zirconium mainly substitutes for titanium. In the backscattered image of figure 2, there are a few light grey areas. Chemical analysis was also performed on these areas and we found a zirconium concentration that was about the same as the bright phase. The relative abundance found in the grey and bright phases of the present investigation agrees with the ones previously reported [15].

The backscattered radiation micrographs of all samples taken at the same magnification are presented in figure 3. We see that, for each composition, the microstructure is made up of four phases: a grey phase, a light grey phase, a bright phase, and a black phase. The composition of each of these phases was evaluated for each composition.

Table 3 presents the atomic composition of the grey phase for all alloys. It is clear that the grey phase has the TiFe stoichiometry in which only a small amount of Zr could be dissolved in a solid solution. This composition stays constant, even with an increasing bulk Zr content. This means that when the bulk content of Zr increases, other phases rich in Zr have to be formed.

The composition of the light grey phase is listed in table 4. We see that the light grey phase has a high zirconium content, but the main element is titanium and is constant for all compositions. In the case of Zr and Fe, the composition is almost constant when the bulk abundance of Zr is more than 8 wt.%, therefore, the stoichiometry of this phase is close to Ti\(_3\)Fe\(_2\)Zr.

The composition of the bright phase is given in table 5. For this phase, contrary to the grey and light grey phases, the proportion of zirconium increases with the increasing X value. In parallel, the proportion of titanium increases and the one for iron decreases.

### 3.2. Crystal structure

The x-ray diffraction patterns of the as-cast alloys are shown in figure 4. For all alloys, the main phase is TiFe. For \(x = 4\), small peaks are barely visible. They are most likely coming from the secondary phases. The secondary phase peaks are more visible for the alloy \(x = 8\). Thermo-Calc calculations
show that along the TiFe bcc phases, there was a presence of a hcp phase. The crystal structure of Fe₂Ti is hcp, as well as a ternary phase Fe₂Ti₀.₈Zr₀.₂, as determined by Surowiec et al. Therefore, we included a hcp phase (space group P6₃/mmc, structure type MgZn₂) in the Rietveld refinement. The fit is not perfect and some peaks are still unindexed.

In the same way, the patterns of \(x = 12\) and \(x = 16\) have some peaks that could be indexed to a hcp phase, but the fit is incomplete and unindexed peaks are still present. Due to the small intensities of these peaks, it was impossible to determine the crystal structure of the secondary phases. Other methods, such as neutron diffraction, may shed some light on the crystal structure of these alloys. In any case, for all alloys the TiFe phase could be fitted. The lattice parameter of the TiFe phase and crystallite sizes, as determined from peak broadening, are reported in table 6.

Inspection of table 6 indicates that the lattice parameter and crystallite size do not change with increasing X. This is in agreement with the constant atomic composition of TiFe phase reported in table 3.

3.3. First hydrogenation

The first hydrogenation kinetics of all the as-cast alloys are presented in figure 5. As shown in earlier works, the hydrogenation of undoped TiFe is essentially impossible to perform without prior activation treatment [14–16]. Therefore, in this investigation we only studied doped TiFe alloy.

Figure 5 shows that increasing the doping fraction from 4 to 8 wt.% had the effect of greatly increasing the reaction kinetics and also increasing the hydrogen capacity. A further increase from 8 to 12 wt.% increased the hydrogen capacity, but there is the appearance of a short incubation time. We also see a change of kinetics at around 1.5 wt.% of hydrogen capacity, which may indicate the absorption of a second phase. With doping of 16 wt.% of Zr, the hydrogen capacity is equal to the theoretical capacity of TiFe (1.9 wt.%), but the incubation time is very long (more than 11 h). There is also a slight change of rate at around 1 wt.% of capacity. Again, this may be an indication that the main TiFe phase and the zirconium-rich secondary phases do not have the same intrinsic
hydrogenation kinetics. But, as the capacity is quite close to the capacity of bare TiFe, we expect that the secondary phase hydrogen capacity is very close to the capacity of TiFe. We are now undertaking an investigation to measure the hydrogen capacity of the secondary phase and to probe the interplay between the TiFe phase and the secondary phase during hydrogenation.

In order to explain the behaviour shown in figure 5, we have to consider the results presented in tables 3–5. From these tables, we see that the atomic composition of the TiFe matrix, as well as the light grey phase, is essentially constant, while the composition of the bright phase changed greatly. From figure 1, we also know that the proportion of the light grey and bright phases increased with an increasing proportion of zirconium. Therefore, it seems that the secondary phase (light grey and bright phases) facilitates the first hydrogenation when they are in relatively small proportion, and when they are in too large a proportion, there is the appearance of an incubation time. More specifically, as the composition of the light grey phase does not change but the one of the bright phase varies, it could be that the phase responsible for the incubation time is the bright phase.

A possible explanation of the behaviours shown in figure 5 could be the following. For $x = 4$ and 8, the amount of secondary phases is relatively small. The small scale of the secondary phases means that, upon hydrogenation, the hydrogen could easily diffuse through the secondary phases and enter the TiFe phase. Proof of the rapid hydrogenation of the secondary phase is the quick absorption up to 0.2 hydrogen wt.% shown for the $x = 4$ alloy. For $x = 8$, the proportion of secondary phases is higher, but the size is still relatively small (a few microns). Thus, the secondary phases still act as a gateway for hydrogen to reach the TiFe phase. For $x = 12$, the island of secondary phases is much bigger. Also, the chemical composition of the bright phase is different than for $x = 4$ and 8. This may be the cause of a small incubation time. However, the intrinsic kinetic (absorption rate after incubation time) is as fast as for $x = 8$. There is also the appearance of a kink in the curve at hydrogen content 1.5 wt.% at $x = 16$, there is a long incubation time, which may be due to the large amount of secondary phases with dimension greater than 20 microns. After incubation, the absorption is very fast, but the kink in the curve is now at around 1 wt.%.

Because of the high hydrogen capacity, it is clear that all phases present in these alloys (TiFe, light grey, and bright) absorb hydrogen. In order to get experimental proof of the possible mechanism proposed above, we are now pursuing a neutron in situ experiment to confirm which phase absorbs hydrogen first.

4. Conclusion

In this paper, we have reported on an investigation to understand the mechanism of fast first hydrogenation in alloys of composition TiFe $+ x$ wt.% Zr ($x = 4, 8, 12, 16$). We found that the as-cast alloys are made up of a TiFe phase with two zirconium-rich secondary phases. The TiFe phase could only accommodate about 1 at.% of Zr irrespective of the $x$ value. As the $x$ value increases, the amount of secondary phases increased. One of the two secondary phases kept the same composition for all values of $x$, while the chemical composition of the other changed. These secondary phases played an essential role in the enhancement of first hydrogenation kinetics and hydrogen capacity. It is clear that all these phases absorb hydrogen and that the secondary phases acted as a hydrogen gateway for the hydrogenation of the TiFe phase.

Figure 4. X-ray diffraction patterns of as-cast alloys TiFe $+ x$ wt.% Zr for $x = 4, 8, 12, and 16$.

Table 6. Lattice parameter and crystallite size of the TiFe phase in as-cast TiFe $+ x$ wt.%Zr alloy ($x = 4, 8, 12, and 16$). Uncertainties on the last significant digit are reported in parentheses.

| Composition | Lattice parameter $a$ (Å) | Crystallite size (nm) |
|-------------|-------------------------|----------------------|
| 4 wt.% Zr   | 2.9826(2)               | 27.1(3)              |
| 8 wt.% Zr   | 2.9802(3)               | 24.1(4)              |
| 12 wt.% Zr  | 2.9836(3)               | 24.3(4)              |
| 16 wt.% Zr  | 2.9813(3)               | 24.3(6)              |

Figure 5. First hydrogenation kinetics at room temperature and under 4500 kPa of hydrogen of as-cast alloys TiFe $+ x$ wt.% Zr for $x = 4, 8, 12, and 16$.
However, the exact role of each secondary phase is still unknown. In situ neutron diffraction experiments may give essential information on the behaviour of each phase during hydrogenation.

Acknowledgment

Part of this investigation was supported by a NSERC Natural Sciences and Engineering Research Council of Canada grant. C G thanks the FRQNT (Fonds de Recherche Nature et Technologies) for a PhD fellowship. J H thanks CAPES/CNPQ for a visiting scientist fellowship (Project number 401400/2014-0, MEC/MCTI/CAPES/CNPQ/FAPS - PVE 2014).

References

[1] Reilly J J and Wiswall R H 1974 Formation and properties of iron titanium hydride Inorg. Chem. 13 218–22
[2] Sandrock G 1999 A panoramic overview of hydrogen storage alloys from a gas reaction point of view J. Alloys Compd. 293–5 877–88
[3] Hotta H et al 2007 Synthesis of Ti–Fe alloys by mechanical alloying J. Alloys Compd. 439 221–6
[4] Bershadsky E, Klyuch A and Ron M 1995 Hydrogen absorption and desorption kinetics of TiFe0.8Ni0.2H Int. J. Hydrog. Energy 20 29–33
[5] Buschow K H J and Miedema A R 1978 Hydrogen absorption in rare earth intermetallic compounds Hydrides for Energy Storage ed A F A J Maeland (Oxford : Pergamon) pp 235–49
[6] Bowman R C, Attalla A and Tadlock W E 1977 NMR-studies of structure and diffusion in metal-hydrides Int. J. Hydrog. Energy 1 421–6
[7] Lee S M and Perng T P 1994 Effect of the 2nd phase on the initiation of hydrogenation of TiFex1–xM, (M = Cr, Mn) alloys Int. J. Hydrog. Energy 19 259–63
[8] Nagai H, Kitagaki K and Shoji K 1987 Microstructure and hydriding characteristics of FeTi alloys containing manganese J. Less-Common Met. 134 275–86
[9] Nagai H, Kitagaki K and Shoji K-I 1988 Hydrogen storage characteristics of FeTi containing zirconium Trans. Japan Inst. Met. 29 494–501
[10] Sicking G and Jungblut B 1983 Surface TiHn as the catalytically active species for the hydrogen absorption by TiFe; a SX-APS investigation supplemented by AES Surf. Sci. 127 255–70
[11] Emami H et al 2015 Hydrogen storage performance of TiFe after processing by ball milling Acta Mater. 88 190–5
[12] Edalati K et al 2014 Activation of TiFe for hydrogen storage by plastic deformation using groove rolling and high-pressure torsion: Similarities and differences Int. J. Hydrog. Energy 39 15589–94
[13] Takahashi K and Isobe S 2014 Enhancing the hydrogen storage capacity of TiFe by utilizing clusters Phys. Chem. Chem. Phys. 16 16765–70
[14] Jain P, Gosselin C and Huot J 2015 Effect of Zr, Ni and Zr5Ni10 alloy on hydrogen storage characteristics of TiFe alloy Int. J. Hydrog. Energy 40 16921–7
[15] Gosselin C and Huot J 2015 Hydrogenation properties of TiFe doped with zirconium Materials 8 7864–2
[16] Jain P et al 2015 Hydrogenation properties of TiFe with Zr5Ni10 alloy as additive J. Alloys Compd. 636 375–80
[17] Lv P and Huot J 2016 Hydrogen storage properties of TiFe with Zr5Ni10 alloy as additive Int. J. Hydrog. Energy 41 22128–33
[18] BRUKER_AXS, TOPAS V5 2014 General profile and structure analysis software for powder diffraction data (Karlsruhe, Germany)
[19] Surowiec Z et al 2003 Investigations of microscopic magnetic properties of the pseudo-binary system (Zr1–xTix)Fe2 J. Phys.: Condens. Matter 15 6403–14