Original Article

Effect of cooling rate on the microstructure and hydrogen storage properties of TiFe with 4 wt% Zr as an additive

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Abstract

In this paper, we report the effect of cooling rate on the microstructure and hydrogenation behaviour of TiFe alloy with 4 wt% Zr as an additive. An ingot of TiFe +4 wt% Zr was synthesized by induction melting, using industrial grade Fe and Ti. Step mold with a thickness of 25, 13, 6 and 3 mm were used to obtain different cooling rates. It was found that higher cooling rate leads to a rapid solidification and finer distribution of the secondary phase. There was no effect of cooling rate on the chemical composition of the different phases present in all thicknesses. However, faster cooling rate leads to faster first hydrogenation kinetics. The reason is that the scale of the secondary phase decreases with increasing cooling rates. The decrease in the scale of the secondary phase was evidenced by the measure of its perimeter. During activation, the hydrogenation rate limiting step for all alloys was found to be 3D growth, diffusion controlled with decreasing interface velocity. The gateway mechanism for the enhanced first hydrogenation kinetics has been confirmed.

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1. Introduction

Use of renewable energies is the solution to solve the problem of climate change [1,2]. Hydrogen is a promising candidate for future energy carrier for mobile and stationary applications due to its light weight, high energy density, and basically generation of only water as a byproduct [3–5]. There are three main ways to store hydrogen: gaseous [6], liquid [7] and solid state [8]. However, liquid and gaseous hydrogen storages are not ideal for most practical applications due to the costly process involved to maintain a cryogenic temperature for liquid hydrogen and the need of high pressurized tank for the gaseous form. Solid-state storage is a safe method to store hydrogen in a compact form. Metal hydrides can store hydrogen reversibly at temperatures between 25 and 350 °C under pressure of the order of a few tens of bars [9,10]. However, metal hydrides should be cost-effective for commercial use. To fulfill this criterion, TiFe alloy is a good candidate because it could operate at room temperature and low pressure [11–14]. However, to

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obtain full capacity and reasonable kinetics, there is a need for an activation step, which is usually a heat treatment of the alloy at high temperature. This breaks the oxide layer formed at the surface of the alloy [15,16].

The activation step can be improved by the addition of a catalyst or dopants such as Zr [17–19], Pd [20], or Ni [21]. Effect of partial substitution of Fe by other transition elements such as Ni, Mo, Cr, and Co on the electrochemical properties of TiFe based alloys was shown by Szajek et al. [22]. Recently, Leng et al. found that introduction of small amount of Ce to TiFe_{0.9}Mn_{0.1} alloys remarkably improved activation properties and it made possible hydrogen absorption at 353 K under an initial hydrogen pressure of 4.0 MPa [23]. Altering microstructure by severe plastic deformation such as high-pressure torsion [24–26], plastic deformation using groove [27] or cold rolling [28] and annealing [29,30] are other ways to ease the activation step. Aoyagi et al. studied the effect of ball milling on the hydrogen absorption curve of TiFe, which results in reducing particle size and creating a new surface for absorption without any prior activation step [31]. Edalati et al. showed the influence of microstructure on the activation of TiFe alloy by formation of cracks and grain boundaries using high-pressure torsion [32]. Vega et al. investigated the effect of cold rolling on the hydrogen storage properties of TiFe [28]. They found that cold rolling of TiFe alloy in inert atmosphere leads to a rapid hydrogen absorption at room temperature. All these processes resulted in getting finer microstructure and lead to better activation kinetics of TiFe alloy.

The cooling rate is also an important parameter during synthesis of alloys for determining the microstructure [33,34]. Higher cooling rate leads to less solidification time and reduces the grain size of the cast alloy and thus increasing grain density [35]. To our knowledge, there are no previous investigations in which effect of cooling rate on the hydrogenation behaviour of TiFe alloy has been reported.

From previous investigations, it is known that addition of 4 wt% Zr enhances the activation (first hydrogenation) kinetics of TiFe alloy [17,18,36,37]. It was also found that the microstructure plays an important role in the beneficial effects of the zirconium-rich secondary phase in this alloy. For industrial scale synthesis, it is important to know the effect of cooling rate on the microstructure and thereby on the hydrogen storage properties. In this investigation, we studied the effect of cooling rate on hydrogen storage properties of TiFe with 4 wt% Zr as an additive. In order to be as close as possible to the industrial process, industrial grade raw materials were used instead of laboratory grade elements.

### 2. Experimental procedure

Ingots of TiFe +4 wt% Zr were synthesized under vacuum using a Consarc induction skull melting furnace (ISM). The size of the melt was 6.5 kg. Industrial steel grade (AISI 1005), commercially pure titanium (ASTM B265 grade 1) and zirconium alloy 702 (99.2 wt% Zr) were used as raw material. Firstly, Fe was melted then Ti and Zr were added to synthesize the alloy. For varying the cooling rate, a ductile cast iron type mold of 25, 13, 6 and 3 mm thickness was used (Fig. 1). The size of the cast part was 225 mm in length and 100 mm wide. The mold was placed in the chamber in the upright position. Temperature was taken with an infrared pyrometer from the top of the vacuum chamber. However, it should be pointed out that copper water cooled ISM (induction skull melting) does not permit giving high superheat to the melt. A balance between the heat extraction of the copper mold and the heat input by the induction happens and a superheat of only 75–150°C can be obtained depending on the melt composition, i.e.: its heat conduction and coupling with the induction. As for the shrinkage in the cast part, the mold was designed so that the shrinkage was happening in the riser. Four samples at different cooling rates were prepared. All ingots of different thicknesses were crushed in air into small chunks. These chunks were converted into powder in a gloves box using a hardened steel mortar and pestle and filled in the reactor in argon atmosphere. The powders were not sieved before filling in the reactor. In order to reduce the cost of metal hydride, the ideal situation would be to have the first hydrogenation being performed under the same conditions as the working conditions of the alloy. Therefore, in this paper, the first hydrogenation (thereafter called activation) was performed at room temperature under 20 bars of hydrogen on a homemade Sievert apparatus. The sample size was of the order of 1 g and the
sample holder temperature was controlled via an air furnace. No previous heat treatment was performed.

Before activation, all samples were kept in a dynamic vacuum for 1 h at room temperature. X-ray diffraction (XRD) patterns of all alloys were recorded using Panalytical X’Pert Pro (PW 3050/60) with Co kα source. XRD analysis was performed on powdered sample. The microstructure of all alloys and the chemical composition of each phase were recorded using Hitachi SU-3500 scanning electron microscope equipped with an EDX (Energy Dispersive X-ray) Spectrometer from Oxford Instruments. Metallographic observations were made in the cross-section of the ingots. All samples were polished before observation. For each phase and each sample, four small areas have been analyzed in order to estimate the uncertainty and reproducibility. The perimeter of the secondary phase was evaluated by using Image J software [38]. Topas software was used for Rietveld refinement of the XRD pattern of all alloys [39].

### 3. Result and discussion

#### 3.1. Morphology

Backscattered micrographs of as-cast TiFe +4 wt% Zr alloy for different thicknesses of mold representing different cooling rates are shown in Fig. 2. It is clear that the microstructure depends on the cooling rate. For 3 mm thickness, a fine dendritic structure is clearly seen. This dendritic structure grows coarser at each step starting with a dendritic arm spacing (DAS) of only a few microns to close to 50 microns at the biggest step. This is directly linked to the different cooling rate, i.e.: higher heat extraction leads to smaller dendrites formation. It could be seen that, in each micrograph, three different phases are present; (1) grey phase (2) light grey phase and (3) bright phase (at the edge of light grey phase).

For the same area covered by the secondary phase, a smaller dendritic structure has more interface with the main phase than a bigger structure. For all samples, the perimeters of the secondary phase over the total area of micrograph were evaluated using the 100 μm scale micrographs. Results are reported in Table 1 and clearly show that the perimeter of the secondary phase increases with increasing cooling rates. Area fraction of grey, light grey, and bright phases has also been calculated by Image J and shown in Table 1. The grey phase area fraction is constant except for the 3 mm thickness.

The phase’s chemical compositions were measured by EDX. Fig. 3 shows the EDX analysis and mapping of 25 mm thickness sample. Areas 1, 2 and 3 respectively represent the grey, light grey, and bright phases. From mapping, it could be seen that Ti is abundant in the grey phase but deficient in light grey and bright phases. Iron (Fe) is evenly distributed through all phases but Zr is mainly concentrated in light grey and bright phases. Identical phases and similar distribution of elements were seen for the 13, 6 and 3 mm thicknesses as in the case of 25 mm thickness.

Chemical compositions of grey phase in each thickness are shown in Table 2. Grey phase has an almost equal atomic concentration of Fe and Ti with a small amount of Zr. Atomic percentages of Ti, Fe, and Zr are essentially the same for the different cooling rate and it is clear that this phase is TiFe alloy.

The chemical compositions of the light grey phase for all thicknesses are given in Table 3. As for TiFe phase, this phase has a constant composition with cooling rates. The stoichiometry of this phase is very close to TiFe, a compound that is present in the Ti-Fe phase diagram. This phase also contains 3 % of zirconium.

Chemical compositions of the bright phase for all thicknesses are shown in Table 4. Here, there is a slight variation in the chemical composition with thickness, but overall, we could consider that this phase composition is roughly constant except for the 3 mm thickness, which contains less zirconium than the other three thicknesses. As this Zr-rich, bright phase is located at the interface between the grey and the light grey phases, we could conclude that zirconium tends to be excluded from the TiFe and the TiFe₂ phases. A close inspection of the abundances given in Table 4 seems to indicate that this region has a composition (Ti, Zr)₂Fe. The compound Ti₂Fe is not present in the phase diagram but it has been seen in the titanium-iron-boron system [40]. As we could see in Fig. 3, bright phase area is very small, only a few % of the total surface.

### Table 1 – Perimeter of the secondary phase over the total area of micrograph as calculated by Image J software.

<table>
<thead>
<tr>
<th>Thickness (mm)</th>
<th>Perimeter (μm/μm²)</th>
<th>Grey phase area (%)</th>
<th>Light grey + bright phase area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>3.6 ± 0.4</td>
<td>60 ± 1</td>
<td>40 ± 1</td>
</tr>
<tr>
<td>13</td>
<td>6.1 ± 0.6</td>
<td>63 ± 1</td>
<td>37 ± 1</td>
</tr>
<tr>
<td>6</td>
<td>10 ± 1</td>
<td>65 ± 1</td>
<td>35 ± 1</td>
</tr>
<tr>
<td>3</td>
<td>25 ± 3</td>
<td>50 ± 1</td>
<td>50 ± 1</td>
</tr>
</tbody>
</table>

### Table 2 – Chemical composition of grey phase (Area 1) of TiFe +4 wt% Zr at the different cooling rate. Uncertainty on all values is ± 1 at. %.

<table>
<thead>
<tr>
<th>Element</th>
<th>25 mm</th>
<th>13 mm</th>
<th>6 mm</th>
<th>3 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti (at. %)</td>
<td>51</td>
<td>50</td>
<td>50</td>
<td>51</td>
</tr>
<tr>
<td>Fe (at. %)</td>
<td>49</td>
<td>49</td>
<td>49</td>
<td>49</td>
</tr>
<tr>
<td>Zr (at. %)</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

### Table 3 – Chemical composition of light grey phase (Area 2) of TiFe +4 wt% Zr at the different cooling rate. Uncertainty on all values is ± 1 at. %.

<table>
<thead>
<tr>
<th>Element</th>
<th>25 mm</th>
<th>13 mm</th>
<th>6 mm</th>
<th>3 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti (at. %)</td>
<td>39</td>
<td>38</td>
<td>38</td>
<td>38</td>
</tr>
<tr>
<td>Fe (at. %)</td>
<td>58</td>
<td>59</td>
<td>59</td>
<td>59</td>
</tr>
<tr>
<td>Zr (at. %)</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

### Table 4 – Chemical composition of bright phase (Area 3) of TiFe +4 wt% Zr at the different cooling rate. Uncertainty on all values is ± 1 at. %.

<table>
<thead>
<tr>
<th>Element</th>
<th>25 mm</th>
<th>13 mm</th>
<th>6 mm</th>
<th>3 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti (at. %)</td>
<td>44</td>
<td>47</td>
<td>44</td>
<td>46</td>
</tr>
<tr>
<td>Fe (at. %)</td>
<td>39</td>
<td>35</td>
<td>36</td>
<td>41</td>
</tr>
<tr>
<td>Zr (at. %)</td>
<td>17</td>
<td>17</td>
<td>20</td>
<td>12</td>
</tr>
</tbody>
</table>
Fig. 2 – Backscattered micrographs of TiFe + 4 wt% Zr at different step mold thickness (a) 25 mm, (b) 13 mm, (c) 6 mm and (d) 3 mm.

Fig. 3 – EDX analysis with mapping of an alloy having a 25 mm thickness of step mold.
3.2. Structural characterization

The crystal structure for samples coming from different thicknesses was determined by analyzing the XRD pattern. Fig. 4 shows the XRD pattern of each sample in the as-cast state. The major diffraction peaks for all thicknesses were found to be TiFe (space group Pm-3m). There are some minor peaks of low intensity, which could be indexed as TiFe₂ type (space group P6₃/mmc) and Ti (space group P6₃/mmc). The small shoulder on the right side of the main TiFe peak is a TiFe₂ peak. The TiFe is the grey phase seen in the SEM micrographs while the TiFe₂ is the light grey phase. The absence of the bright phase in the X-ray patterns could be explained in two ways. First, the area of this phase in the SEM micrographs is very small, only a few % of the total surface. Therefore, it is at the limit of detection for X-ray diffraction. Secondly, from the SEM observation and EDX measurements, this phase is most likely related to the light grey phase. Also, the peak at around 45° could be indexed to the Ti phase but, after Rietveld refinement, there is still a non-negligible residue. Moreover, one could notice a series of very small peaks between 75 and 93°. These peaks may belong to the bright phase, but the intensities are so small and the peaks are so broad, it makes a precise identification impossible.

The Rietveld analysis was performed on each alloy’s XRD pattern and the R-values are given in Table 5. The relatively high value of Rwp is probably due to the relatively high background of these patterns as discussed by Toby [41].

The main parameters determined by Rietveld refinements are summarized in Table 6. Phase fraction of each phase presented in Table 6 is on weight basis. Pure zirconium phase was also considered during the Rietveld analysis, but this phase is not present in any pattern. We see that the phase fraction of TiFe is practically constant except for the 6 mm sample that is slightly higher. The Ti fraction increases with cooling rates and the fraction of TiFe₂ has one value for the 25 and 13 mm samples and smaller value for the 6 and 3 mm samples. For all cooling rates, the individual phases have different crystallite size, but they do not change much with cooling rates. For all phases, microstrains were found to be zero within experimental errors.

From Table 6, it could be seen that the lattice parameters of the TiFe₂ range from a = 4.91 to 4.95 nm, c = 7.00 to 7.24 and the c/a ratio from 1.43 to 1.48. The c/a ratio is particularly problematic. This number is too far from the theoretical value of a hexagonal phase. This is a strong indication that the structure is metastable. Other possible phases were tested but the TiFe₂ structure was the one giving the best fitting. However, as the peaks are relatively small and the peaks quite broad, it makes the identification quite difficult.

3.3. Activation kinetics

Activation (first hydrogenation) curves of TiFe with 4 wt% Zr at different cooling rates are shown in Fig. 5. It is clear that the activation kinetics increases with cooling rates. This is most likely due to the finet distribution and large perimeter of the secondary phase as cooling rate increases. There is also less diffusion distance between the secondary phase and the center of the TiFe phase.

The total capacity gives some indication of the hydrogenation reaction. For example, for the 3 mm sample, the total capacity reached was 1.4 wt%. Considering that, from Rietveld refinement, TiFe phase is 61% and that TiFe absorbs 1.86 wt.%

| Table 5 – The weighted profile factor R-factor (Rwp) and the expected R-factor (Rexp) in Rietveld’s analysis for each alloy. |
|-----------------|-----------------|-----------------|
| Thickness (mm) | Rwp            | Rexp            |
| 25              | 13.07          | 9.18            |
| 13              | 12.20          | 9.57            |
| 6               | 14.98          | 9.65            |
| 3               | 13.87          | 11.28           |

<table>
<thead>
<tr>
<th>Table 6 – Phase fraction, lattice parameter and crystallite size of each alloy having different thicknesses.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase name</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>25 mm</td>
</tr>
<tr>
<td>TiFe</td>
</tr>
<tr>
<td>TiFe₂</td>
</tr>
<tr>
<td>Ti</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>13 mm</td>
</tr>
<tr>
<td>TiFe</td>
</tr>
<tr>
<td>TiFe₂</td>
</tr>
<tr>
<td>Ti</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>6 mm</td>
</tr>
<tr>
<td>TiFe</td>
</tr>
<tr>
<td>TiFe₂</td>
</tr>
<tr>
<td>Ti</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>3 mm</td>
</tr>
<tr>
<td>TiFe</td>
</tr>
<tr>
<td>TiFe₂</td>
</tr>
<tr>
<td>Ti</td>
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<tr>
<td></td>
</tr>
</tbody>
</table>
of hydrogen then, the amount of hydrogen taken by the TiFe phase is 1.13 wt.%. The missing capacity is due to the secondary phase (TiFe₂ and Ti). As the missing capacity is only 0.27 wt. % and the secondary phases are counting for 39 wt.%. This means that these phases absorbed only a small amount of hydrogen. The preceding analysis found that the secondary phases are TiFe₂, Ti₂Fe, and Ti. It is known that the TiFe₂ phase does not absorb hydrogen [42]. It leaves the Ti₂Fe and Ti phases, which are possible hydrogen absorbers. Titanium forms a hydride, but the amount formed is too small to be accurately detected by X-ray. As for the Ti₂Fe phase, there is some evidence by SEM/EDX, but the amount is not sufficient to be seen on the XRD pattern. Therefore, more dedicated experiment is needed in order to determine secondary phase absorbs hydrogen and what is the capacity.

One way to check the reversibility of these alloys would be to perform desorption and absorption/desorption cycles. This will be part of a following paper.

The shape of activation curves could give some information about the hydrogenation mechanism. Table 7 shows the usual models of rate-limiting steps in hydrogenation. As different models have different functional forms, one way to find the model that fits our experiments is to plot the left side of the equations as a function of time. The model that fits the best will give a straight line. In these equations, X is the transformed fraction, which is the ratio of the absorbed quantity of hydrogen divided by the sample’s maximum hydrogen absorption capacity (X = [%H/[%Hₘₐₓ]), while k and t are respectively the rate constant and time. The linear regression was performed from 10 to 90% of the transformed fraction (X = [0.1…0.9]) and the results are shown in Fig. 6 for the 3 mm thickness.

At 3 mm thickness, the best linear fitted plot is for the GB3D, 3D growth, diffusion controlled with decreasing interface velocity model. GB3D was also found to be the best-fitted model for the other thicknesses.

The rate constant of the reaction for each thickness is shown in Table 8. Rate constant value increases with increasing cooling rate (decrease in mold thickness). The relationship between the rate constant and perimeter of the secondary phase is shown in Fig. 7. It is clear that the rate constant is linearly proportional to the perimeter. It has already been shown by Edalati et al. that grain boundaries, vacancies concentration, and high dislocation density acts as a pathway for hydrogen diffusion [27,32]. In the present case, the activation mechanism is at the interface between the TiFe phase and the secondary TiFe₂ phase. From the measured and calculated hydrogen capacity, we could conclude that the secondary phase absorbs only a small amount of hydrogen. Thus, it acts as a gateway for hydrogen. In previous work, we found that the phases present in the as-cast alloy were metastable and heat treatment was responsible for the effect of changing the nature of the secondary phase and also the metastability of the phases, which had for the consequence of drastically reducing the activation kinetics and total capacity [46]. The present result agrees with these conclusions. In the as-cast state the phases are in a metastable state and thus, probably have an unstable boundary between them. Such an unstable boundary could provide an easy diffusion of hydrogen between the
4. Conclusion

The effect of cooling rate on TiFe alloy doped with 4 wt% Zr was studied by using step casting. Casting was done at a scale of a few kg in order to be as close as possible to the industrial process. The raw materials were also industrial grade. The cast alloy consisted of a main TiFe phase and a zirconium-rich secondary phase. It was observed that cooling rate had an influence on the alloy's microstructure. Fast cooling rates produced a dendritic structure with fine distribution of the secondary phase. Slower cooling rates produced a coarser structure for the secondary phase. However, the chemical composition of each phase was essentially constant with respect to cooling rates.

In this work it was shown that activation kinetics of as-cast alloys has a clear increase in the reaction rate with increasing cooling rates. The reaction rate was found to be proportional to the secondary phase perimeter and the rate-limiting was identified to be diffusion controlled for all cooling rates. The fact that the rate of the first hydrogenation kinetic is proportional to the perimeter between the TiFe phase and the secondary phase is a strong indication of the gateway mechanism of hydrogen entering first the secondary phase and then transfer to the main TiFe phase.

Conflicts of interest

The authors declare no conflicts of interest.

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