Original Article

Effect of ball milling and cryomilling on the microstructure and first hydrogenation properties of TiFe+4 wt.% Zr alloy

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\begin{abstract}
In this paper, we report the microstructure and first hydrogenation properties of TiFe cast with 4 wt.% of Zr. Measurements were made in as-cast state and after processing by ball milling and cryomilling. It was found that ball milling and cryomilling significantly reduced the particle/crystallite sizes with most of the reduction occurring during the first 15 min of milling. While the cryomilled sample did not absorb any hydrogen, ball milling improved the initial kinetics of processed powders compared with the as-cast sample. However, it also reduced the hydrogen storage capacity. The observed increased kinetics was likely caused by the reduction of crystallite sizes with longer ball milling times. However, the longer ball milling times might also have been the reason of the capacity loss due to formation of new grain boundaries. Faster kinetics was not due to a change in the rate-limiting step, as all kinetics curves were fitted with the 3D growth, diffusion controlled with decreasing interface velocity model.

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\end{abstract}

1. Introduction

The TiFe alloy is a good material for solid state hydrogen storage due to its low plateau pressure at room temperature and relatively low price [1–7]. However, one of its disadvantages is rather slow first hydrogenation kinetics [8–11]. Reilly et al. reported that pure TiFe sample had to be exposed to high temperatures (around 400 °C) and high hydrogen pressures (6.5 MPa) before being able to absorb/desorb hydrogen at normal conditions [12]. Thus, one way to reduce the cost of this alloy is to make its first hydrogenation possible at room temperature and under low hydrogen pressure.

Doping is an effective way to improve the hydrogenation properties of the TiFe alloy. Kumar et al. found that the first hydrogenation of TiFe sample doped with 3.1 wt.% of vanadium occurred at 54 °C. However, hydrogen storage capacity slightly decreased [13]. Later, Jain et al. showed that...
the first hydrogenation of the TiFe alloy was possible without any prior heat treatment just by adding zirconium [14]. Recently, Lv and Huot found that Ti$_{0.95}$FeZr$_{0.05}$, TiFe$_{0.95}$Zr$_{0.05}$ and TiFeZr$_{0.05}$ alloys showed totally different microstructures and the first hydrogenation properties. The first hydrogenation (also called activation) of these alloys was performed at room temperature and under 2 MPa of hydrogen gas [3].

Mechanical milling is also an effective method to improve the first hydrogenation properties of the TiFe alloy. It is well known that presence of defects and nanocrystallites could enhance the reaction kinetic and reduce incubation time. Moreover, it has been shown that mechanical milling is a fast and efficient way to reduce crystallite sizes and induce defects in materials [1,7,15,16]. Chiang et al. investigated the hydrogenation properties of TiFe alloy processed under the reactive hydrogen atmosphere. They found that milled TiFe powder absorbed hydrogen without any prior heat treatment [17]. Emami et al. used ball milling technique to synthesise the nanocrystalline TiFe metallic compound. Their study showed clearly that ball milling reduced the particle sizes of processed powders and facilitated the first hydrogenation reaction [1].

Recently, Gosselin et al. found that the first hydrogenation of the TiFe alloy doped with 4 wt.% of zirconium occurred at room temperature and under 4.5 MPa of hydrogen gas [18]. Joydev et al. also found that the hydrogen capacity of air exposed TiFe+4 wt.% zirconium alloy can be recovered by cold rolling and ball milling. However, the hydrogen absorption process was still too slow [19]. The objective of our investigation is to improve the kinetic of the first hydrogenation of TiFe based alloy. The effect of ball milling and cryomilling TiFe alloy with addition of 4 wt.% of zirconium is investigated in detail in the present work. The hypothesis was that ball milling or cryomilling will introduce defects that will help the hydrogenation kinetics. However, ball milling could also destroy/change the microstructure of this two phase alloy and may end up being detrimental. In this investigation, ball milling was done under argon as usual but cryomilling was performed in air. The reason for cryomilling in air was that a recent investigation showed that cold rolling in air enhance the first hydrogenation of TiFe+4 wt.% of zirconium [19]. Milling in air could then be easier to compare with cold rolling.

2. Materials and methods

Fe (99.9%), Ti (99.9%) and Zr (99.5%) were purchased from Alfa Aesar and used without further purification. TiFe+4 wt.% Zr was prepared by arc melting in argon atmosphere. All samples were synthesized by mixing the three elements at the proper ratio and melting them together. In order to improve the sample homogeneity, each pellet was turned over and remelted three times. Ball milling was performed on as-cast alloys using hardened stainless-steel balls, with a ball to powder (BTP) weight ratio of 10:1. Loading of the crucible was done in an argon-filled glovebox. Ball milling was performed for 5, 15, 30 and 60 min (simplified samples notation: BM5, BM15, BM30 and BM60, respectively) with a SPEX 8000M apparatus at the milling velocity of 1060 rpm. Powders handling and milling were done in argon. Cryomilling (simplified sample notation: CM15) was performed in a hardened steel vial using a Retsch CryoMill at liquid nitrogen temperatures, with a BTP ratio of 20:1. The milling was carried out continuously for 15 min, at the impact frequency of 30 Hz (1800 rpm). For cryomilling, powders handling and milling were done in air.

The crystal structure was determined by powder X-ray diffraction (PXD) using a Bruker D8 Focus diffractometer ($\lambda = \text{CuK}_\alpha$). Lattice parameters were calculated by Rietveld refinements using the TOPAS software [20,21]. Microstructural and chemical analysis of powders were carried on with a JEOL JSM-5500 scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS). The hydrogen storage properties were measured using a home-made Sieverts-type apparatus.

3. Results and discussion

3.1. Morphology

Fig. 1 shows the SEM micrographs of the as-cast, ball milled and cryomilled samples of TiFe+4 wt.% Zr alloy. The as-cast particles have sharp edges, resulting from the grinding procedure performed using a mortar and a pestle. After only 5 min of ball milling, the particles are much smaller and are characterized by round edges. Further milling resulted in agglomerations of smaller particles. Cryomilling produced a much finer powder without the agglomeration seen in the room temperature milling.

3.2. Phase analysis and microstructure

The PXD patterns for ball milled and cryomilled samples of the TiFe+4 wt.% Zr alloy are presented in Fig. 2. It can be clearly seen that the TiFe Bragg peaks (PDF#65-5613) of the ball milled powders are getting broader with longer milling times. This is an indication of the crystallite size reduction due to mechanical processing of the materials. The low-intensity peaks at around 38–46° 2θ in the diffraction pattern of the as-cast sample are due to the secondary phase (Fe$_3$Ti with MgZn$_2$-type structure, PDF#65-0602) [22]. They are no longer observed in the PXD data of the ball milled samples because the peaks broadening due to reduction of crystallite size makes them indistinguishable from the background.

Table 1 shows the calculated lattice parameters and crystallite sizes for all samples. The lattice parameter seems to have an erratic behavior but it should be mentioned that the literature value of the lattice parameter of TiFe varies from a lower boundary of 2.953(2) Å [23] to a upper boundary of 2.9802(2) Å [24]. In the present case, the lattice parameter is actually higher than the high boundary literature value but is agrees with the value recently published on for TiFe+4 wt.% Zr alloys [25]. The observed minor expansion of the unit cell can be explained by the presence of a small amount of Zr in solid solution in the TiFe lattice. Table 1 indicates that the crystallite size is reduced with prolonged milling. Results also show that 15 min of cryomilling leads to formation of bigger crystallites
than milling for the same time at room temperature. This can be explained by the fact that the milling conditions (milling atmosphere, milling speed, BTP ratio, balls sizes, etc.) were totally different in both experiments.

3.3. First hydrogenation

Fig. 3 shows the first hydrogenation process at room temperature and under 4.5 MPa of hydrogen. The as-cast alloy absorbed 1.6 wt.% of H₂ in 2.5 h. Ball milling slightly improved the hydrogenation kinetics of the reaction but the capacity decreased with milling times. Even more drastic effect is seen for the cryomilled sample that did not absorb any hydrogen. This may be explained by the fact that the experiment was carried out in air and resulted in the formation of oxide(s) layer on the surface of particles. Due to that, cryomilling as short as 15 min, made the alloy totally inert toward hydrogen. There is no evidence of oxide in the powder diffraction powder of the cryomilled sample. However, usually the oxide layer is very thin (a few nm) and has a small abundance. These two facts make the Bragg peaks very weak and quite broad. This makes them essentially indistinguishable from the background. More evidence should be collected to prove the presence of the oxide layer but, as a first hypothesis, we assume that it is the reason for the inertness of this sample toward hydrogen.

Why samples with longer ball milling times show faster kinetics but lower hydrogen storage capacity should also be explained. In Fig. 1 and Table 1 it can be seen that...
longer milling time at room temperature effectively reduce the crystallite/particle sizes. This leads to a faster diffusion of hydrogen along the particle surfaces and the newly formed grain boundaries. In addition, the latter are favorable nucleation sites for the formation of the hydride phase [26]. This may explain the initial fast absorption kinetics of the ball-milled samples.

Table 2 presents the total hydrogen capacity (wt.%) of powders hydrogenated for 5 h, and the capacity retention (%) for all samples. The capacity retention is defined as the measured capacity over the theoretical capacity of TiFe (1.86 wt.%). It is easy to see that the capacity retention decreases with increasing ball milling times. In their investigation of ball milled magnesium hydride, Hanada et al. explained that the decreased crystallite size associated with increasing grain boundary and lattice strains can lead to the decrease in hydrogen storage capacity [27]. This phenomenon appears to be also present in our sample. Fig. 4 shows the dependence of the total hydrogen capacity and the crystallite size on the ball milling time for the TiFe+4 wt.% Zr alloy. As can be seen, with the longer milling time the crystallite size and the total hydrogen capacity decrease in the same fashion.

Fig. 4 gives a qualitative relationship between crystallite size and capacity. However, a more precise description is possible. In their investigation, Emami et al. also mentioned that the width of the grain boundaries in ball milled TiFe is close to 0.3 nm and proposed that grain boundaries may act as trapping sites for the hydrogen [1]. Upon milling, crystallite size is reduced which means that new grain boundaries are created. In the model shown in Fig. 5, we assumed that all crystallites are spherical and all grain boundaries have a thickness of 0.3 nm. We could then calculate the relative volume of the grain boundary with respect to the total volume. Presuming that the capacity loss was entirely due to formation of new grain boundaries, the expected capacity loss due to creation of new grain boundaries could be calculated. Results are shown in Table 3. The value $V_{gb}/V_{total}$ is the ratio of grain boundary volume over the total volume and is considered to be the expected capacity loss due to formation of grain boundaries. The hypothesis is that the grain boundaries are acting as diffusion path for hydrogen thus accelerating the kinetics but, hydrogen is not stored in the grain boundaries and therefore brings the capacity loss that is proportional to the grain boundary volume. The expected loss due to the presence of grain boundaries is remarkably close to the measured capacity loss. As pointed out by Emami et al., a grain boundary of 0.3 nm is the same size as the TiFe unit cell. This means that, reduction of crystallite size is simply due to the coherency break on one unit cell which is the definition of a crystallite size. In order to confirm this hypothesis other proofs are needed such for example TEM.
3.4. Rate limiting step models of first hydrogenation

The first hydrogenation curves were analyzed by comparison with different rate limiting step models shown in Table 4. For all models, the left side of the equations is a function of the reaction’s completion ratio \( \alpha(t) \) (\( \alpha = \%H_{abs}/\%H_{max} \)), \( t \) is the reaction time, and \( k \) is the kinetic rate constant. In order to find the correct rate limiting step, the left side of these equations was plotted as a function of time. From this type of plot, the correct rate limiting step is a linear curve.

As a representative, Fig. 6 shows the plot of the first hydrogenation kinetic for the alloy milled 5 min (BM5). Linear regressions were performed on each model. As indicated in the literature, the regressions were made in the range from 10% to 90% of the reaction’s completion (\( \alpha = 0.1–0.9 \) [28]). Fig. 7 shows the residue plots for linear fits of rate limiting step calculations for Fig. 6. And it can be clearly seen that GB3D model clearly shows a very flat curve in Fig. 7. This means that GB3D shows a good fit. In addition, Table 5 shows the adjusted \( R^2 \) values for all rate limiting step model equations. For GB3D this value is 0.946 and indicates a very linear curve. This means that the GB3D model describes the best rate limiting

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size (radius/nm)</th>
<th>( V_{GB}/V_{total} ) (%)</th>
<th>Capacity loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As cast</td>
<td>11.6</td>
<td>7</td>
<td>12</td>
</tr>
<tr>
<td>BM5</td>
<td>5.2</td>
<td>15</td>
<td>17</td>
</tr>
<tr>
<td>BM15</td>
<td>4.2</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>BM30</td>
<td>2.8</td>
<td>26</td>
<td>30</td>
</tr>
<tr>
<td>BM60</td>
<td>2.4</td>
<td>30</td>
<td>31</td>
</tr>
</tbody>
</table>

Table 4 – Rate limiting step model equations [28,29].

<table>
<thead>
<tr>
<th>Model name</th>
<th>Model equation where ( \alpha ) is ( %H_{abs}/%H_{max} )</th>
<th>Model description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemisorption</td>
<td>( \alpha = kt )</td>
<td>Surface controlled</td>
</tr>
<tr>
<td>JMA2D</td>
<td>( \lceil\ln(1 - \alpha)\rceil^{1/3} = kt )</td>
<td>2D growth of existing nuclei with constant interface velocity</td>
</tr>
<tr>
<td>JMA3D</td>
<td>( \lceil\ln(1 - \alpha)\rceil^{1/2} = kt )</td>
<td>3D growth of existing nuclei with constant interface velocity</td>
</tr>
<tr>
<td>CV2D</td>
<td>( (1 - \alpha)^{1/3} = kt )</td>
<td>2D growth of with constant interface velocity</td>
</tr>
<tr>
<td>CV3D</td>
<td>( (1 - \alpha)^{1/2} = kt )</td>
<td>3D growth of with constant interface velocity</td>
</tr>
<tr>
<td>GB2D</td>
<td>( (1 - \alpha)\ln(1 - \alpha) + \alpha = kt )</td>
<td>2D growth, diffusion controlled with decreasing interface velocity</td>
</tr>
<tr>
<td>GB3D</td>
<td>( 1 - (2\alpha/3) - (1 - \alpha)^{1/3} = kt )</td>
<td>3D growth, diffusion controlled with decreasing interface velocity</td>
</tr>
</tbody>
</table>
step for the sample milled for 5 min. From the description given in Table 4, the GB3D model assumes a 3D growth and the growth interface velocity of diffusion decreases with time [30]. Similar plots were made for the first hydrogenation curves of all samples. The results indicate that the activation kinetics agree with the GB3D model for all of them.

4. Conclusion

Hydrogenation properties of mechanochemically processed TiFe with addition of 4 wt.% of Zr has been investigated. The as-cast sample shows TiFe as a main phase and traces of Fe₂Ti-like phase. Results of the first hydrogenation on samples that were processed by ball milling and cryomilling lead to the following conclusions:

(1) Ball milling and cryomilling significantly reduce the particle/crystallite sizes with most of the reduction occurring during the first 15 min of milling. In addition, ball milling produced particle agglomeration which increases with milling times.

(2) High energy milling at room temperature improves the initial hydrogenation kinetics of processed powders as compared with the as-cast sample but reduces the H-storage capacity. The faster kinetics is due to the reduction of the crystallite sizes and formation of new grain boundaries. The reduced hydrogen storage capacity may be explained by the formation of grain boundaries that enhance the hydrogen diffusion but do not store hydrogen in their structures.

(3) Cryomilled sample does not absorb any hydrogen. Although there is no hard proof of the presence of oxide layer in this powder, it is very likely that it is the reason for inertness toward hydrogen.

(4) The first hydrogenation kinetics for all samples agrees well with the GB3D model. The feature of this model is that the 3D growth and the growth interface velocity of diffusion decrease with time.

Conflicts of interest

The authors declare no conflicts of interest.

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REFERENCES

[3] Lv P, Huot J. Hydrogen storage properties of Ti 0.95 FeZr 0.05, TiFe 0.95 Zr 0.05 and TiFeZr 0.05 alloys. Int J Hydrogen Energy 2016;41:22128–33.