Original Article

Effect of high zirconium content on hydrogenation properties and anti-poisoning ability of air-exposed TiFe alloy

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\textbf{A B S T R A C T}

In order to improve the anti-poisoning ability of air-exposed TiFe alloy, the TiFe + x wt.% Zr (x = 8, 12 and 16) alloys were synthesized by arc melting and subsequently exposed in air for different time. The results show that all samples handled in air can absorb the hydrogen directly without any incubation time. In addition, their first hydrogenation kinetics increases with the proportion of zirconium. And for the samples exposed in air for 35 h, all samples also can absorb the hydrogen without any heating and mechanical treatment, but x = 8 sample needs a long incubation time. Further study, it can be found that each alloy exposed in air for 35 h includes three phases: a TiFe main phase with very small amount of zirconium, a hcp secondary phase with high proportion of zirconium and very small titanium phase. Also, more hcp secondary phases are beneficial for the improvement of the first hydrogenation kinetics but also lead to higher loss of capacity after first absorption and desorption. Above results suggest that introducing high zirconium content can improve the anti-poisoning ability of TiFe alloy effectively. This may be because that the bright phase (hcp phase) probably can\textdaggerdbl; be oxidized as easily as the dark phase (TiFe phase).

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1. Introduction

The rapid development of fuel cell vehicles promotes the development of hydrogen production \cite{1-9} and hydrogen storage \cite{4-7} technologies. TiFe alloy is considered to be an efficient hydrogen storage material because it can operate at room temperature and mild hydrogen pressure \cite{8-12}. However, TiFe alloy is very easy to lose reaction activity when it is exposed to the air. It has been found that the formation of stable oxide layer on the surface that can forbid the diffusion of hydrogen into the TiFe bulk \cite{10,13-17}. Therefore, TiFe alloy usually needs a harsh activation (so-called the first hydrogenation) condition including high temperature conditions.
(around 673 K) and high pressure (around 6–7 MPa) [18–20]. In order to solve such problems, researchers came up with two main approaches including using mechanical deformation (ball milling [9,14,21,22], cold rolling [10,13,14], high pressure torsion [23,24], equal channel angular pressing [25–27]) and adding or substituting transition elements (V [28,29], Mn [11,18,30,31], Zr [15,32–34], Co [35], Al [35,36] and Ni [15,35]).

For so many transition elements, introducing zirconium is a good way to improve the first hydrogenation properties of TiFe alloy. Jain et al. [15] found that adding 4 wt.% zirconium to TiFe alloy can reduce the temperature and hydrogen pressure of first hydrogenation due to the effect of zirconium-rich secondary phase. Manna et al. [14] reported that TiFe +4 wt.% zirconium is thoroughly dead when it is exposed in air. But its first hydrogenation can be recovered by cold rolling or ball milling. Despite air-exposed TiFe +4 wt.% zirconium can be activated again after cold rolling and ball milling. But the treating processes will lead to the loss of capacity and the cost of time.

Recently, Gosselin et al. [33,37] studied the first hydrogenation properties of TiFe +x wt.% Zr (x = 4, 8, 12 and 16) alloy in argon atmosphere. They found that adding zirconium can efficiently improve the first hydrogenation kinetics of TiFe alloy at room temperature and 4.5 MPa hydrogen. Despite the large progress in shortening the incubation time, but the results reported are only performed in argon atmosphere. In addition, this study does not provide much attention at all to the anti-poisoning ability of these alloys. So it is difficult for us to understand the effect of air exposure on the hydrogenation properties of TiFe alloy by adding zirconium. Therefore, the main objective of this study is to investigate the effect of air exposure on hydrogenation properties and anti-poisoning ability of TiFe by adding high zirconium content.

### 2. Experimental details

#### 2.1. Preparation of the alloy

In this paper raw iron (99.9%), titanium (99.9%) and zirconium (99.5%) materials were purchased from Alfa Aesar. Before the arc melting, the surface of iron was polished to remove the rust by the sandpapers. TiFe and TiFe +x wt.% Zr (x = 8, 12 and 16) alloys were prepared by arc melting in argon atmosphere using single melt method [33]. Each pellet was remelted and turned over four times. In order to see the effect of different air exposure time, three types of air exposure were made as shown in Fig. 1: one handled in argon, called (HC-Ar), one only crushed in air, indicated (HC-air) and one crushed and exposed in air for 35 h (HC-35). For HC-35, the samples were crushed in air by using a mortar and placed in vials without lid in air for 35 h before the experiment.

#### 2.2. Hydrogenation measurement

Hydrogenation kinetics were done at room temperature under 2.0 MPa hydrogen pressure without any prior heating or mechanical treatment. The PCT curves was measured at room temperature under 0.1–2.5 MPa. These measurements were done by using a home-made Sieverts-type apparatus.

### Table 1 – Rate limiting step model equations [50,51].

<table>
<thead>
<tr>
<th>Model name</th>
<th>Model equation, α is %H_{\text{Alm}}/%H_{\text{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>$\ln([\text{H}_2]/[\text{H}_2]) + \frac{1}{2} = kt$</td>
<td>2D growth of existing nuclei with constant interface velocity</td>
</tr>
<tr>
<td>JMA3D</td>
<td>$\ln([\text{H}_2]/[\text{H}_2]) + \frac{1}{2} = kt$</td>
<td>2D growth with constant interface velocity</td>
</tr>
<tr>
<td>CV2D</td>
<td>$\ln([\text{H}_2]/[\text{H}_2]) + \frac{1}{2} = kt$</td>
<td>3D growth with constant interface velocity</td>
</tr>
<tr>
<td>CV3D</td>
<td>$\ln([\text{H}_2]/[\text{H}_2]) + \frac{1}{2} = kt$</td>
<td>3D growth, diffusion controlled with decreasing interface velocity</td>
</tr>
<tr>
<td>GB2D</td>
<td>$\ln([\text{H}_2]/[\text{H}_2]) + \frac{1}{2} = kt$</td>
<td>3D growth, diffusion controlled with decreasing interface velocity</td>
</tr>
<tr>
<td>GB3D</td>
<td>$\ln([\text{H}_2]/[\text{H}_2]) + \frac{1}{2} = kt$</td>
<td>3D growth, diffusion controlled with decreasing interface velocity</td>
</tr>
</tbody>
</table>

Fig. 1 – The schematic diagram of TiFe + x wt.% Zr (x = 8, 12 and 16) alloys using different processing treatments.
2.3. **Morphology analysis**

Morphology and composition analysis were done by using a JEOL JSM-5500 scanning electron microscopy equipped with an EDX (Energy Dispersive X-Ray) apparatus. The area of dark and bright phases was measured by using image J software [38,39].

2.4. **Crystal structure analysis**

The crystal structure was measured by X-ray diffraction (Bruker D8 Focus; Cu Kα radiation). The crystallite size was evaluated from Rietveld method using GSAS 2 software [40].

3. **Results and discussion**

3.1. **First hydrogenation of HC-air**

The first hydrogenation kinetics of TiFe and TiFe + x wt.% Zr (x = 8, 12 and 16) alloys handled in air under an initial hydrogen pressure of 2 MPa at room temperature is shown in Fig. 2. As can be seen from this figure, no absorption of the hydrogen was detected in pure TiFe alloy even after 3000 s. The other samples (x = 8, 12, 16) can absorb the hydrogen in a very short incubation time (<10 s) without any heating treatment process although they were handled in air. In addition, the maximum hydrogen capacity also increased with x. This indicated that adding zirconium can improve the first hydrogenation kinetics and anti-poisoning ability of TiFe alloy. But the reaction rate and maximum hydrogen capacity were lower than the result of Gosselin et al. [33,37]. It should be noted that Gosselin et al. prepared all samples in argon atmosphere and measured the first hydrogenation kinetics under 4.5 MPa of hydrogen.

In order to understand the change of first hydrogenation mechanism of TiFe + x wt.% Zr (x = 8, 12 and 16) alloys handled in air, the first hydrogenation curves for all samples were analyzed by using different rate limiting step models including nucleation-growth-impingement model (JMA) [41,42], contracting volume model (CV) [43-46] and ginstling-Brounshtein model (GB) [47,48] in Table 1. The left side of the equation is a function of the reaction completion ratio (a).

Fig. 3 shows the rate limiting step curves of first hydrogenation of x = 8 handled in air. It can be seen clearly that each curve can be divided into two sections: one from about 140 s to 750 s
and the other one from about 750 s to 2700 s. Linear fit for each rate limiting step curve in first and second sections is shown in Fig. 4 (Sections 1 and 2). In order to find the best fit, the adjusted $R^2$ value for each model of Sections 1 and 2 in Fig. 4 is shown in Table 2. It is clear that the rate limiting step is GB3D model for two sections. From the description of GB3D model in Table 1, it is 3D growth and the growth interface velocity of diffusion decreases with time.

Fig. 5 presents the rate limiting step curves of first hydrogenation of $x = 12$ handled in air. Similar with $x = 8$, we also can find that each curve includes two sections: one from about 190 s to 800 s and the other one from about 800 s to 3200 s. Linear fit for each rate limiting step curve in first and second sections is shown in Fig. 6 (Sections 1 and 2). The adjusted $R^2$ value for each model of Sections 1 and 2 in Fig. 6 is shown in Table 3. Combining with Fig. 6 and Table 3, we can see clearly that the rate limiting step of Section 1 is CV3D model, which presents 3D growth with constant interface velocity. For Section 2, GB3D model is indicated in Table 3. The change of rate limiting step model may explain why the reaction rate obviously decreases in Section 2.

The rate limiting step curves of first hydrogenation of $x = 16$ handled in air is shown in Fig. 7. Same time, each curve is made of two parts. The period of Section 1 is between around 190 s and 480 s and the period of Section 2 is from around 480 s to 1350 s. Linear fit for each rate limiting step curve in first and second sections is shown in Fig. 8 (Sections 1 and 2). The adjusted $R^2$ value for each model of Sections 1 and 2 in Fig. 8 is shown in Table 4. For Section 1, it is clear that CV3D model shows the best fit. For Section 2, CV3D switches to GB3D model. This means that $x = 16$ has similar first hydrogenation mechanism with $x = 12$.

3.2. First hydrogenation properties of HC-35

In this experiment, the as-crushed sample was kept in a vial without a lid for 35 h in air. The first hydrogenation kinetics of TiFe + x wt.% Zr (x = 8, 12 and 16) alloys exposed in air for 35 h under an initial hydrogen pressure of 2 MPa at room temperature is shown in Fig. 9. As can be seen from this figure, all samples can absorb the hydrogen after the period of incubation time, but $x = 8$ needs a long incubation time (around 3000 s). In addition, the hydrogen capacity and reaction rate still increase with $x$ like the samples handled in air, but the reaction rate is slower.

In order to compare the difference of first hydrogenation properties, the hydrogen capacity (wt.%) and incubation time (s) of different samples in different states (HC-Ar, HC-air and HC-35) are shown in Table 5. From this table, we can clearly see that the prolonged air exposure time results in the reduction of hydrogen capacity and increase of incubation time for all samples. In addition, the short air exposure (HC-air) barely has effect on the incubation time but the long air exposure time (HC-35) can drastically promote the incubation time. We take the attitude that the longer incubation time and lower hydrogen capacity may be due to denser oxide layer (TiO$_2$/FeO$_x$) formed by air exposure which makes the hydrogen diffusion hard [12,14]. During different air exposure time, $x = 16$ still shows the highest hydrogen capacity and shortest incubation time. This proves that adding high zirconia can resist the effect of air exposure on TiFe alloy effectively. In previous researches, Jain et al. [15] studied TiFe + 4 wt.% Zr alloy handled in air and found that the incubation time of this alloy needed around 1500 s and maximum hydrogen capacity only reached 1.3 wt.% of hydrogen. Aoyagi et al. [52] also reported that ball-milled TiFe alloy can absorb any hydrogen after only 0.2 Ks air exposure. Compared with these reports, the present result shows the significant improvement of the anti-poisoning ability of TiFe alloy by adding high zirconium content. The significant improvement leads us to study investigate the crystal structure and morphology of the samples after air exposure for 35 h.

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**Table 2 – Adjusted $R^2$ values for all model equations of Sections 1 and 2 in Fig. 4.**

<table>
<thead>
<tr>
<th></th>
<th>Chemisorption</th>
<th>JMA2D</th>
<th>JMA3D</th>
<th>CV2D</th>
<th>CV3D</th>
<th>GB2D</th>
<th>GB3D</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 12$ Section 1</td>
<td>0.94741</td>
<td>0.9507</td>
<td>0.92996</td>
<td>0.97171</td>
<td>0.97821</td>
<td>0.99456</td>
<td>0.99476</td>
</tr>
<tr>
<td>$x = 12$ Section 2</td>
<td>0.92044</td>
<td>0.96721</td>
<td>0.96185</td>
<td>0.95556</td>
<td>0.96509</td>
<td>0.96072</td>
<td>0.9703</td>
</tr>
</tbody>
</table>
Fig. 5 – The rate limiting step curves of first hydrogenation of x = 12 handled in air.

Table 3 – Adjusted \( R^2 \) values for all model equations of Sections 1 and 2 in Fig. 6.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Adjusted ( R^2 )</th>
<th>Chemisorption</th>
<th>JMA2D</th>
<th>JMA3D</th>
<th>CV2D</th>
<th>CV3D</th>
<th>GB2D</th>
<th>GB3D</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 12 Section 1</td>
<td>0.98241</td>
<td>0.9812</td>
<td>0.96715</td>
<td>0.99403</td>
<td>0.99643</td>
<td>0.98826</td>
<td>0.98489</td>
<td></td>
</tr>
<tr>
<td>x = 12 Section 2</td>
<td>0.88851</td>
<td>0.94891</td>
<td>0.94142</td>
<td>0.93407</td>
<td>0.94676</td>
<td>0.94238</td>
<td>0.95501</td>
<td></td>
</tr>
</tbody>
</table>

Table 4 – Adjusted \( R^2 \) values for all model equations of Sections 1 and 2 in Fig. 8.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Adjusted ( R^2 )</th>
<th>Chemisorption</th>
<th>JMA2D</th>
<th>JMA3D</th>
<th>CV2D</th>
<th>CV3D</th>
<th>GB2D</th>
<th>GB3D</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 12 Section 1</td>
<td>0.96714</td>
<td>0.97366</td>
<td>0.95919</td>
<td>0.98432</td>
<td>0.98825</td>
<td>0.98556</td>
<td>0.98355</td>
<td></td>
</tr>
<tr>
<td>x = 12 Section 2</td>
<td>0.89891</td>
<td>0.94951</td>
<td>0.94387</td>
<td>0.93574</td>
<td>0.94628</td>
<td>0.9396</td>
<td>0.95066</td>
<td></td>
</tr>
</tbody>
</table>

Table 5 – Hydrogen capacity (wt.%) and incubation time (s) of different samples in different states.

<table>
<thead>
<tr>
<th>Sample</th>
<th>HC-Ar [37]</th>
<th>HC-air</th>
<th>HC-35</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Capacity (wt.%)</td>
<td>Incubation time (s)</td>
<td>Capacity (wt.%)</td>
</tr>
<tr>
<td>8</td>
<td>1.70</td>
<td>0</td>
<td>1.61</td>
</tr>
<tr>
<td>12</td>
<td>1.85</td>
<td>1</td>
<td>1.65</td>
</tr>
<tr>
<td>16</td>
<td>1.90</td>
<td>11</td>
<td>1.79</td>
</tr>
</tbody>
</table>
3.3. Crystal structure of HC-35

Fig. 10 shows the XRD patterns of TiFe+X wt.% Zr (x=8, 12 and 16) alloys exposed in air for 35 h. Even if the samples were exposed in air for 35 h, but the peaks of oxide phases cannot be observed in the XRD pattern [13,14]. We can clearly see that all samples show TiFe (Pm-3m), hcp (P63/mmc, MgZn2 type) and Ti (Im-3m) phase. There is a little difference from the result reported by Gosselin et al. [33,37], which only identified TiFe and hcp (P63/mmc, MgZn2 type) phases. For Ti phase, this is probably due to the more substitution of Zr atom to Ti atom with increasing X, which leads to the presence of redundant Ti. This result agrees with the report by Shang et al. [8], who also found Ti phase in the crystal structure of as-cast Ti1.1Fe0.5Mn0.2, alloy.

Table 6 shows the crystallite size (nm) of TiFe phase of TiFe+X wt.% Zr (x=8, 12 and 16) alloys exposed for 35 h in air as determined by Rietveld analysis. It can be clearly seen that the crystallite size of TiFe phase increases with X. According to the previous literature [14], for air exposed sample, the crystallite size is smaller than for the as-cast sample. This is due to the formation of oxide can reduce the average crystallite size of TiFe phase. So at this point, we can explain that adding more zirconium can effectively prevent the formation of oxide but results in a little bigger average crystallite size as shown in Table 6.

3.4. Morphology of HC-35

Fig. 11(a, b, c) shows the backscattered electron micrographs of TiFe+X wt.% Zr (x=8, 12 and 16) alloys exposed in air for 35 h, respectively. Fig. 11 (d) shows the relationship between the bright phase area (%) and x (wt.%). It should be noted here that all samples for backscatter measurement were some small pieces without any polish. It can be seen that each micrograph mainly shows a two-phase microstructure including bright and dark phases. Using image J software, the propor-
Fig. 9 – The first hydrogenation kinetics of TiFe + x wt.% Zr (x = 8, 12 and 16) alloys exposed in air for 35 h at room temperature under 2 MPa hydrogen pressure.

### Table 6 – Crystallite size (nm) of TiFe phase of TiFe + x wt.% Zr (x = 8, 12 and 16) alloys exposed for 35 h in air as determined by Rietveld analysis.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Parameters</th>
<th>x = 8</th>
<th>x = 12</th>
<th>x = 16</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiFe</td>
<td>Crystallite size</td>
<td>24.7(3)</td>
<td>25.7(7)</td>
<td>26.1(1)</td>
</tr>
</tbody>
</table>

Fig. 10 – The XRD of TiFe + x wt.% Zr (x = 8, 12 and 16) alloys exposed in air for 35 h.

Table 7 – EDX analysis of TiFe + x wt.% Zr (x = 8, 12 and 16) alloys in the dark phase (point A).

<table>
<thead>
<tr>
<th>Element (Atomic%)</th>
<th>x = 8</th>
<th>x = 12</th>
<th>x = 16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>49.3</td>
<td>47.6</td>
<td>48.7</td>
</tr>
<tr>
<td>Ti</td>
<td>49.7</td>
<td>51.4</td>
<td>50.1</td>
</tr>
<tr>
<td>Zr</td>
<td>1.1</td>
<td>1.0</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table 8 – EDX analysis of TiFe + x wt.% Zr (x = 8, 12 and 16) alloys in the bright phase (point B).

<table>
<thead>
<tr>
<th>Element (Atomic%)</th>
<th>x = 8</th>
<th>x = 12</th>
<th>x = 16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>52.5</td>
<td>49.1</td>
<td>40.9</td>
</tr>
<tr>
<td>Ti</td>
<td>37.9</td>
<td>36.7</td>
<td>37.1</td>
</tr>
<tr>
<td>Zr</td>
<td>9.6</td>
<td>14.2</td>
<td>21.9</td>
</tr>
</tbody>
</table>

Table 9 – First and second hydrogen capacity and loss of capacity (wt.%) of different samples exposed in air for 35 h.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Capacity (wt.%)</th>
<th>Loss of capacity (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First</td>
<td>Second</td>
</tr>
<tr>
<td>8</td>
<td>1.30</td>
<td>0.88</td>
</tr>
<tr>
<td>12</td>
<td>1.38</td>
<td>0.80</td>
</tr>
<tr>
<td>16</td>
<td>1.79</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Tables 7 and 8 show the EDX analysis of the dark phase (point A) and bright phase (point B) respectively. Analysis of the dark phase (Table 7) indicates that for x = 8, 12, and 16,
zirconium content is very low. The ratio of titanium and iron seems to be 1:1. The means that the dark phase has similar TiFe stoichiometry only with zirconium in solid solution state. Inspection of the bright phase (Table 8), it can be seen that titanium abundance is constant over the whole range of x values and iron is substituted by zirconium when x increases. In addition, zirconium shows very high abundance (around 10%). Further study, we find that the composition of bright phase can match the hcp phase similarly.

Fig. 12 presents the schematic diagram of effect of bright phase on the hydrogen diffusion of TiFe+x wt.% Zr (x=8, 12 and 16) alloys exposed in air for 35 h at room temperature under 2 MPa hydrogen pressure. It has been reported that adding zirconium can produce the bright phase which can enhance the first hydrogenation kinetics in argon atmosphere [15,32,33,37]. This conclusion also supports the samples exposed in air. As shown in Fig. 9, all samples exposed in air for 35 h can still absorb the hydrogen with increasing zirconium content without any heating or mechanical treatment. However, why can introducing zirconium improve the anti-poisoning ability of TiFe alloy? It can be explained from Fig. 12. There are three layers made of the alloy, hydrides and oxide in the schematic diagram. When the alloy is exposed in air, the oxide layer is formed on the surface of the alloy. But the bright phase (hcp phase) probably cannot be oxidized as easily as the dark phase (TiFe phase) [14]. This means that there may be no or less oxide layer in the area of bright phase. So adding more zirconium can lead to more bright phases, which
form more non-oxide areas. As we know from these previous studies [14,32,33], the presence of bright phase is a gateway for hydrogen to reach the TiFe phase. Even if the TiFe with adding high zirconium alloy is exposed in air, but it is still easy for hydrogen atoms to diffuse quickly through the bright phase area without oxide layer.

3.5. Second hydrogenation properties of HC-35

Fig. 13 shows the second hydrogenation of TiFe + x wt.% Zr (x = 8, 12 and 16) alloys exposed in air for 35 h at room temperature under 2 MPa hydrogen pressure. Prior to the measurement, the samples were kept under vacuum for 0.5 h at room temperature. It can be seen clearly that the second hydrogenation show faster reaction rate than the first hydrogenation. They can reach around 75% hydrogen capacity in only 60 s. This may be due to the destroy of the oxide layer in the dark phase area after the first hydrogenation, which provides a lots of diffusion paths for hydrogen atoms. But it is also very clear that the hydrogen capacity is lower for the second hydrogenation than the first hydrogenation.

Fig. 13 – Second hydrogenation curves of TiFe + x wt.% Zr (x = 8, 12 and 16) alloys exposed in air for 35 h at room temperature under 2 MPa hydrogen pressure.

Fig. 14 – The relationship of loss of capacity, bright phase area and zirconium content x of different samples exposed in air for 35 h.
Table 9 shows the first and second hydrogen capacity and loss of capacity of different samples exposed in air for 35 h. We can see clearly that the loss of capacity increases with zirconium content. In order to see the inner link of capacity and bright phase area, the relationship of loss of capacity, bright phase area and x of different samples exposed in air for 35 h are shown in Fig. 14. It should be very clear that the loss of capacity and bright phase area increase with x synchronously. This indicates that the higher abundance of bright phase may lead to higher loss of capacity.

Further study, we hold the view that the loss of capacity could be explained from two points: one due to the nature of the apparatus, the other one due to the formation of stable hydride phase. For the first point, it could be explained by quite fast second absorption kinetics compared with the first absorption. The nature of the apparatus does not record the first second of the second absorption, which makes the capacity decrease [49]. For the second point, we can give an example of x = 12. If there is no oxidation reaction, taking into account that the hydrogen capacity of TiFe is 1.86 wt.% and that, for x = 12, the amount of TiFe phase (dark phase) is around 51% as determined by SEM in Fig. 11(d), so this phase should contribute to around 0.95 wt.% to the hydrogen capacity. This means that the hcp phase (bright phase) also absorbs hydrogen with a capacity (0.91 wt.%) similar to the TiFe phase. So the bright phase can form the hydrides during the first hydrogenation. According to the literature [15,32], the hydrides formed by bright phase may be very stable, which can’t desorb at room temperature. This leads to the reduction of the hydrogen capacity during the second absorption. More studies need to be done to identify the kind of stable hydrides in the future.

3.6. Pressure-composition isotherms of HC-35

After the first hydrogenation cycle, the pressure-composition isotherm of different samples (x = 8, 12 and 16) were measured at room temperature in Fig. 15. Prior to the measurement, the samples were kept under vacuum for 1 h at room temperature. From Fig. 15, it can be seen clearly that the reversible capacity of these samples decreases with increasing zirconium content, which is opposite to the first absorption kinetics. In addition, the reversible capacity seems to be lower than those measured during the first absorption. A possible reason for the lower reversible capacity may be due to the stable hydrides which can’t dehydrogenate during the first desorption (vacuum for 1 h) at room temperature [15]. This result is also found in the second hydrogenation shown Fig. 13. Further study, it also can be found that the absorption plateau pressures are at around 0.4 MPa and the desorption plateau pressures are at around 0.1 MPa. The lower desorption plateau suggests an increase of hydrides stability, which means that adding zirconium obviously change the thermodynamics of dehydrogenation kinetics.

4. Conclusion

The anti-poisoning ability and hydrogenation properties of air-exposed TiFe alloy by adding high zirconium content have been investigated in this paper. It is shown clearly that adding high zirconium content can effectively improve the anti-poisoning ability of TiFe alloy. The following issues can be summarized.

(1) All samples of HC-air can absorb the hydrogen directly. In addition, their first hydrogenation kinetics increases with
zirconium content. But the rate limiting step is different for each sample. For \( x = 8 \), the both sections are controlled by GB3D. However, for \( x = 12 \) and 16, the first part of the reaction is controlled by CV3D, then switching to GB3D for the second part.

(2) For those samples of HC-35, all samples still can absorb the hydrogen in spite of the long exposure time. The hydrogen capacity and reaction rate increase with zirconium content.

(3) Each sample of HC-35 is multiphase: a TiFe main phase with very small amount of zirconium, a hcp secondary phase with high zirconium and very small titanium phase. More hcp secondary phases can improve the first hydrogenation kinetics but also lead to higher loss of capacity after first absorption and desorption.

(4) Introducing zirconium can improve the anti-poisoning ability of TiFe alloy. It may be explained that the bright phase (hcp phase) probably cannot be oxidized as easily as the dark phase (TiFe phase).

Conflict of interest

The authors declared that they have no conflicts of interest to this work.

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