Magnesium-based hydrogen storage nanomaterials prepared by high energy reactive ball milling in hydrogen at the presence of mixed titanium–iron oxide

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1. Introduction

High Energy Reactive Ball Milling in Hydrogen (HRBM) is a very efficient route for the preparation of hydrogen storage materials on the basis of nanostructured magnesium hydride \((n\text{-MgH}_2)\) [1]. When combined with catalysts, including easily hydrogenated alloys [2], HRBM of Mg has been shown to be a good method for the production of the hydride materials suitable for large-scale weight efficient hydrogen storage [3]. Further improvement on performances of the \(n\text{-MgH}_2\) can be achieved with the addition of carbon which apart from intensification of heat transfer in the MH bed [3], also improves the \(H_2\) absorption/desorption kinetics and operation lifetime, even when the carbon additive loading is below 5 wt.% [4].

There are several solutions to improve the HRBM preparation of MgH\(_2\) and to facilitate dehydrogenation–re-hydrogenation processes. Some of these solutions suggest addition of various metal oxides. Apart from the binary ones, including Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\), Cr\(_2\)O\(_3\), CeO\(_2\), Y\(_2\)O\(_3\), TiO\(_2\), Nb\(_2\)O\(_5\) [5–13], the catalytic effect was also observed for the mixed oxide, NiCo\(_2\)O\(_4\); the improvements were associated with the formation of metallic nanoparticles formed in the course of the oxide reduction [14]. The catalytic effect of the reduced oxide nanoparticles formed during HRBM was also dis-

1. Introduction

An experimental study was undertaken on the preparation, by High Energy Reactive Ball Milling in Hydrogen (HRBM), of hydrogen storage materials on the basis of Mg mixed with FeTiO\(_3\), and their further characterisation (SEM, TEM, XRD, volumetric \(H_2\) absorption studies, TDS). It was shown that the addition of \(\geq 5\) wt.% of FeTiO\(_3\) dramatically improves \(H_2\) absorption in Mg and reduces the temperature of further \(H_2\) desorption. Subsequent addition of carbon, including Graphite (G), Activated Carbon (AC) and Multi-Wall Carbon Nanotubes (MWCNT) results in some slowing of the \(H_2\) absorption down but significantly improves re-hydrogenation performances of the material, which in time is able to re-absorb about 5 wt.% \(H_2\) in less than 5–7 min (15 bar \(H_2\)/250 °C). These improvements were associated with the reduction of FeTiO\(_3\) to yield nanoparticles of Fe and TiFe(H\(_x\)).

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For the composition Mg – 10 wt.% TiFeO₃ additional carbon-containing samples were prepared, by further addition of 0.4 g (5 wt.% as respect to Mg) of carbon, in the form of Graphite (C) powder (Fluka: <20 μm, 99+%); VP-50F Activated Carbon (AC; Kuraray Chemical Co.); and Multi-Wall Carbon Nanotubes (MWCNT; Carbon Nano-Material Technology Co., Ltd.).

HRBM was carried out in Retsch PM100 planetary ball mill using 220 mL hardened steel vial equipped with pressure–temperature monitoring system (Evico Magnetics GmbH), at ball-to-powder ratio, BPR = 40 : 1, and 500 rpm rotation speed. Milling was started at room temperature and H₂ pressure of 30 bar. Both pressure and temperature in the vial were monitored to yield the data on hydrogenation kinetics during HRBM. The milling was interrupted every time when the temperature approached 65°C, or hydrogen pressure dropped below 20 bar; the vial was then cooled down to the room temperature and refilled with H₂ before resuming HRBM.

The characterisation of HRBM and re-hydrogenation products included SEM (Zeiss Auriga Field Emission Gun; InLens (working distance 5 mm) and secondary electron (10 mm) detectors at 5 kV), TEM (FEI Tecnai 30, 120 kV), the sample holder was cooled to liquid nitrogen temperature), and XRD (Bruker AXS D8 Advance, Cu Kα, λ_{1} = 1.5406 Å, λ₂ = 1.5444 Å, 2θ = 10–85°; the data were further processed by Rietveld full-profile analysis using GSAS software, the characteristics of the constituent phases were taken from CRYSMET database [27,28]). TDS (dynamic vacuum; T = 25–470°C, ramp rate 5°C/min) and re-hydrogenation (15 bar H₂/250°C) were carried out using a Sieverts-type volumetric installation; sample weight was of 200 mg.

The re-hydrogenation data were fitted using a modified Avrami–Erofeev equation:

\[ C = C_{\text{max}} \left(1 - \exp \left(-\left(\frac{t}{t_{o}}\right)^{n}\right)\right) \]

where \( C \) and \( C_{\text{max}} \) are the actual and maximum hydrogen concentrations, respectively; \( t \) is time; \( t_{o} \) is a characteristic reaction time; and \( n \) is a parameter ("Avrami exponent") indirectly related to the reaction mechanism.

Further details on the experimental procedure and data processing can be found in [4].

3. Results and discussion

Fig. 1 shows hydrogen absorption kinetics in the studied samples Mg–x FeTiO₃–(5C) during HRBM (A) and re-hydrogenation after TDS (B). The corresponding curves for magnesium without additives (Mg) taken at the same conditions are presented for the reference.

Quite distinct from individual Mg (whose hydrogenation during HRBM is very slow and requires more than 5 h milling to achieve maximum H storage capacity), the samples containing TiFeO₃ require 1–2 h to achieve complete hydrogenation (Fig. 1A). The hydrogenation rates gradually increase with the increase of TiFeO₃ content and at ≥5 wt.% TiFeO₃ the amount of H absorbed during 1 h long HRBM is 5.8–6.7 wt.%. With carbon additives, hydrogenation proceeds slower and is characterised by an incubation period whose duration depends on the type of the additive. Nevertheless, about 7 wt.% H is absorbed during 1 h of HRBM for AC and MWCNT, and during 2 h for graphite.

The presence of FeTiO₃ also improves re-hydrogenation kinetics as compared to HRBM Mg (Table 1). The time (\( t_{o} \)) required to absorb (1 - 1/e) = 63.2% of the total amount of hydrogen (\( C_{\text{max}} \)) in the modified samples gradually decreases from ~25 min for the unmodified HRBM Mg to ~6.5 min for Mg–5 FeTiO₃. Further increase of FeTiO₃ content to 10 wt.% results in slowing the re-hydrogenation down (\( t_{o} \) ~ 14 min), but the reaction is still faster than for the individual HRBM Mg. However, the introduction of FeTiO₃ significantly reduces the total amount of the re-absorbed hydrogen, from ~5 wt.% for HRBM Mg alone to 3.8 wt.% for Mg–2 FeTiO₃ and further to 2.7 wt.% for Mg–10 FeTiO₃. The fitted n values are significantly lower in the Mg–x FeTiO₃ samples (0.32–0.54) than the one for HRBM Mg (0.73) testifying about change of the reaction mechanism.

1 Here and below the notation corresponds to the samples containing x wt.% of FeTiO₃ and, if present, 5 wt.% of carbon (C = C, AC or MWCNT).

The samples additionally modified with carbon additives exhibit higher hydrogen absorption capacities during re-hydrogenation, >5 wt.%, and the kinetics are further improved (Fig. 1B, Table 1). The n values (0.75–1) for the carbon-containing samples are quite close to the one for HRBM Mg, similarly to our earlier observations for HRBM Mg + C [4].

As can be seen from Fig. 2, the introduction of FeTiO₃ significantly lowers the temperatures of the onset and peak of hydrogen desorption. The lowest peak temperature (316°C, or almost 60°C lower than for the HRBM Mg alone) was observed for Mg–10 FeTiO₃. Further introduction of MWCNT does not significantly affect the MgH₂ decomposition temperature. For graphite and activated carbon the peak temperatures were ~20°C higher, but still significantly lower than that of HRBM Mg.

The as-milled samples exhibit typical morphology for HRBM Mg (porous agglomerates of submicron particles) on SEM images [4]; the morphology is similar for the samples with and without carbon additives (compare Fig. 3A and B). As can be observed from the TEM images (Fig. 3C and D), small, ~50 nm particles of TiFeO₃ (or the products of its transformation) are homogenously distributed in the MgH₂ matrix. The re-hydrogenated samples (Fig. 3D) exhibit sintering and twinning, typically for HRBM MgH₂ [4].

More details on the TEM studies are presented in the Supplementary Information.

Examples of the refined XRD patterns are presented in Fig. 4, for the as-milled (A, B) and re-hydrogenated (C, D) samples, respectively. The plots in Fig. 4 correspond to the experimentally
observed (points) and calculated (lines) intensities, as well as the difference (observed–calculated; bottom line). The bottom labels (Fig. 4A, C, D) correspond to the diffraction angles for the peaks calculated for the identified phases (labelled from the left). In all cases the goodness of fit corresponded to $R_p/C25 = 0.02$.

All as-milled samples (Table 2) contain tetragonal $\alpha$- ($P4_2/mmm$, #36; $a = 4.52 \text{ Å}, c = 3.02 \text{ Å}$; [27], record AL2897) and orthorhombic $\gamma$- ($Pbcn$, #60; $a = 4.48 \text{ Å}, b = 5.40 \text{ Å}, c = 4.90 \text{ Å}$; [27], record 506717) modifications of MgH$_2$ as major phases. For Mg–$x$ FeTiO$_3$, both phases exhibit calculated crystallite size between 13 and 17 nm; and the total abundance of MgH$_2$ gradually decreases from 97.4 to 86 wt.% following the increase of FeTiO$_3$ content in the charge. The samples without carbon additives contain a single impurity phase of FeTiO$_3$ ($R-3$; #148; $a = 5.09 \text{ Å}, c = 14.09 \text{ Å}$; [27], record 503413) with lattice periods close to the reference data and crystallite size between 16 and 70 nm. The abundance of FeTiO$_3$ approximately corresponds to the content of the oxide in the charge only at $x \leq 5$ wt.%, and exhibits underestimations by 2.8 wt.% for $x = 10$ wt.%, and by about 6 wt.% for $x = 15$ wt.%.

The introduction of carbon significantly changes phase-structural properties of the as-milled Mg–10 FeTiO$_3$. First, the abundance of FeTiO$_3$ decreases twofold for $C = G$. The samples also exhibit significant amounts of nanocrystalline (~5 nm) MgO ($Fm-3m$, #225; $a = 4.21 \text{ Å}$; [27], record 31985). For $C = AC$, the FeTiO$_3$ phase disappears, and the abundance of MgO increases in 2.3 times as compared to $C = G$; this sample also exhibits the highest abundance of $c$-MgH$_2$.

For the patterns of as-milled Mg–10 FeTiO$_3$–5C, better refinement was obtained assuming appearance of microcrystalline TiF$_x$H$_y$ ($P2_22_1$, #17; $a = 3.09 \text{ Å}, b = 4.52 \text{ Å}, c = 4.39 \text{ Å}$; [27], record 133245) for $C = G$ and nanocrystalline Fe (hexagonal high-pressure modification, hcp-Fe; $P6_3/mmc$, #194; $a = 2.47 \text{ Å}, c = 3.96 \text{ Å}$; [27], record 27813) for $C = AC$. The difference of impurity phases in

<table>
<thead>
<tr>
<th>FeTiO$_3$/carbon (type) (wt.%)</th>
<th>$C_{\text{max}}$</th>
<th>$t_0$</th>
<th>$n$</th>
<th>Pearson correlation coefficient, $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg (no additives)</td>
<td>4.976(1)</td>
<td>23.47(5)</td>
<td>0.731(2)</td>
<td>0.9931</td>
</tr>
<tr>
<td>2</td>
<td>3.781(7)</td>
<td>11.5(1)</td>
<td>0.297(2)</td>
<td>0.9879</td>
</tr>
<tr>
<td>5</td>
<td>2.85(1)</td>
<td>6.43(7)</td>
<td>0.53(4)</td>
<td>0.915</td>
</tr>
<tr>
<td>10</td>
<td>2.71(2)</td>
<td>14.2(5)</td>
<td>0.32(4)</td>
<td>0.9844</td>
</tr>
<tr>
<td>10/5 (G)</td>
<td>5.45(2)</td>
<td>4.87(2)</td>
<td>1.03(5)</td>
<td>0.9923</td>
</tr>
<tr>
<td>10/5 (AC)</td>
<td>5.23(1)</td>
<td>6.52(3)</td>
<td>0.97(4)</td>
<td>0.9860</td>
</tr>
<tr>
<td>10/5 (MWCNT)</td>
<td>5.21(3)</td>
<td>3.20(2)</td>
<td>0.80(7)</td>
<td>0.9665</td>
</tr>
</tbody>
</table>

Fig. 2. Hydrogen Thermal Desorption Spectra (TDS) for the re-hydrogenated HRBM Mg and Mg–10 FeTiO$_3$–(5C). The peak temperatures are specified in brackets.

Fig. 3. SEM (A and B) and bright-field TEM (C and D) images of as milled Mg–10 FeTiO$_3$ (A and C), as milled (B) and re-hydrogenated (D) Mg–10 FeTiO$_3$–5AC.
Mg–10 FeTiO$_3$ and Mg–10 FeTiO$_3$–5C (C = G, AC) can be clearly seen in Fig. 4B where all three patterns are presented together in the range $2\theta = 49–51^\circ$.

TDS followed by re-hydrogenation dramatically changes phase-structural properties of the as-milled materials (Table 3). In all samples Mg–$x$ FeTiO$_3$ the FeTiO$_3$ phase disappears accompanied by the appearance of rather high amount of nanocrystalline MgO whose abundance correlates with the initial content of FeTiO$_3$. All the samples exhibit nanocrystalline $\alpha$-Fe (Im-3m, #229, $a = 2.87$ Å; [27], record 29057) and (except for Mg–2 FeTiO$_3$ and Mg–10 FeTiO$_3$–5G) TiFeH. For the re-hydrogenated samples Mg–10 FeTiO$_3$–5C, the abundance of MgO decreases, as compared to Mg–10 FeTiO$_3$, in 1.8, 2.6 and 3.7 times for C = G, AC and MWCNT, respectively. All carbon-containing re-hydrogenated samples are characterised by the reduction of crystallite size of $\alpha$-MgH$_2$ in 1.5–1.8 times (similar to our earlier observation for HRBM-Mg–C [4]), and significantly lower abundance (or disappearance) of the non-hydrogenated Mg which, if present, has significantly bigger crystallite size than in the samples without carbon. Interestingly, for all re-hydrogenated Mg–10 FeTiO$_3$–5C samples, TiFeO$_3$ was found in the amount of ~3 wt.% while for the as-milled Mg–10 FeTiO$_3$–5AC (Table 1) it was absent.

Analysis of the presented data allows the authors to assume that during dehydrogenation and re-hydrogenation TiFeO$_3$ reacts with magnesium (or magnesium hydride) according to the reactions:

\[
\text{FeTiO}_3 + 3\text{Mg(H}_2) \rightarrow \text{TiFe} + 3\text{MgO (+3H}_2); \tag{2}
\]

\[
\text{FeTiO}_3 + \text{Mg(H}_2) \rightarrow \text{Fe} + \text{MgO} + \text{TiO}_2 (+\text{H}_2). \tag{3}
\]

Since neither TiO$_2$, nor possible product of its interaction with MgO (Mg$_2$TiO$_4$), were detected by XRD, it was assumed that these products of Reaction (3) are amorphous (indirectly confirmed by TEM results; see Fig. S2C in the Supplementary Information). Nevertheless, both reactions resulted in:

(i) generation of metallic nanoparticles which (especially, TiFe) are known to catalyse hydrogen dissociation/recombination and thus improve re-hydrogenation and dehydrogenation kinetics;

(ii) consumption of magnesium to form MgO.

Most probably, Reactions (2) and (3) take place at the end of the dehydrogenation process. At high contents of FeTiO$_3$ ($x \geq 5$ wt.%) they may begin already on the HRBM stage to yield amorphous products. It can be testified by (i) significant increase of the hydrogenation rate during HRBM when FeTiO$_3$ content approaches the threshold value and (ii) underestimation of XRD abundances for FeTiO$_3$ in the as-milled samples. In the presence of carbon, XRD of the as-milled samples (Table 2) directly indicate that the interaction takes place already during HRBM.

In Mg–$x$ FeTiO$_3$, MgO formed by Reactions (2) or (3) covers the Mg particles as a dense film inhibiting their re-hydrogenation,
especially when the formed layer of MgH₂ creates an additional diffusion barrier for hydrogen atoms. HRBM in the presence of carbon was shown to result in the formation of graphene layers encapsulating the MgH₂ nanoparticles [4]. Apart from creating an interface for the migration of active hydrogen species and preventing grain growth of MgH₂, carbon may also alter Reactions (2) and (3) thus maintaining some kind of "equilibrium" between TiFeO₃ from one side and MgO, TiFe and/or TiO₂ + Fe from the other. This results in the less pronounced lowering of the H amount absorbed in the course of re-hydrogenation of the carbon-containing materials.

4. Conclusions

- Addition of FeTiO₃ to Mg results in shorter hydrogenation times during HRBM, improved dehydrogenation and re-hydrogenation kinetics, but reduced reversible H storage capacity of the material.
• During HRBM, dehydrogenation and re-hydrogenation, FeTiO$_3$ reacts with Mg (or MgH$_2$) to yield MgO and nanoparticles of Fe and TiFe(Hx) which are known to catalyse H$_2$ dissociation/recombination and thus improve dehydrogenation and hydrogenation kinetics.

• Further addition of carbon, including graphite, activated carbon and multi-walled carbon nanotubes results in some slowing down of H absorption during HRBM but significantly increases reversible hydrogen storage capacity of the material.

Acknowledgements

This work was supported by the Department of Science and Technology (DST) in South Africa within the HySA Programme (project KP3-S02 – On-Board Use of Metal Hydrides for Utility Vehicles), and Human Resources for Industry Programme, jointly managed by the South African National Research Foundation and the Department of Trade and Industry (NRF/DTI; THRIP project TP1207254249). It is also supported by ERAfrica FP7 program, project RE-037 “HENERGY”. Finally, ML acknowledges NRF support via incentive funding grant 76735.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jallcom.2014.12.084.

References