# Room temperature hydrogen absorption by Mg and Mg–TiFe nanocomposites processed by high-energy ball milling

R.A. Silva [a], R.M. Leal Neto [b], D.R. Leiva [a,*], T.T. Ishikawa [a], C.S. Kiminami [a], A.M. Jorge Jr. [a], W.J. Botta [a]

[a] Departamento de Engenharia de Materiais, Universidade Federal de São Carlos, Rodovia Washington Luiz, km 235, CEP 13565 – 905, São Carlos, SP, Brazil
[b] Instituto de Pesquisas Energéticas e Nucleares (IPEN), Av. Lineu Prestes 2242, Cidade Universitária, CEP: 05508-000, São Paulo, SP, Brazil

## ARTICLE INFO

## ABSTRACT

Mg - 40 wt % TiFe nanocomposite was prepared by high-energy ball milling, HEBM, aiming improved hydrogen absorption at room temperature (RT). Four processing routes were chosen to separately investigate the effects of TiFe addition, HEBM processing and dispersion of TiFe particles, being: Route 1 – mechanical mixture of Mg and TiFe powders; Route 2 – HEBM of Mg + TiFe at 400 rpm for 12 h; Route 3 – HEBM of pure Mg at 400 rpm for 12 h to be used as reference; and Route 4 – HEBM of Mg + TiFe at 600 rpm for 36 h. In this case, TiFe was previously milled with ethanol to improve its refinement level. It is shown that the synergetic effects of TiFe addition, HEBM processing and thermal activation – involving the creation of Mg–TiFe interfaces, the refinement and distribution of TiFe and also the presence of free Fe – lead to good hydrogenation kinetics at RT in Mg–TiFe nanocomposite. It is also shown for the first time that the milled pure Mg can absorb hydrogen at RT.

## Introduction

Hydrogen is a renewable and economically sustainable energy resource. It has been considered as a clean energy carrier, without toxic emissions [1–3]. Aside from conventional applications of hydrogen as in the synthesis of ammonia and methanol, and in the petrochemical industry, due to its high efficiency in generating power, it could be used as future fuel for electric vehicles and power generators as fuel cells. The noticeable advantage of using hydrogen in such applications is an absence of pollution because the only by-product is the water [3–5].

However, the hydrogen applications mentioned above face two crucial issues. Firstly, so far, hydrogen is mainly generated from fossil fuels [6], creating massive volumes of carbon dioxide, which is a notorious greenhouse gas, consequently affecting worldwide warm up and producing the nowadays noticeable clime variations. Furthermore, besides non-renewable, fossil fuels makes the world economically dependent on few geographical areas and large conglomerates.

---

Secondly, deployment of an economical, safe and uncomplicated storage method is an essential condition to promote the broader application of $H_2$ as an energy carrier [7,8]. Traditional methods of storing hydrogen included high-pressure gas cylinders and liquefied hydrogen, which are limited by technological issues as appropriate pressure vessels for compressing hydrogen gas and cryogenic temperatures respectively, beside large sizes and weights [9].

For the sake of solving the first above issue, the production of hydrogen imperatively needs to be substituted by clean and renewable feedstocks [4]. If one thinks about the primitive carbon cycle (without the use of fossil fuels), biomass is being identified as a promising renewable source. By using biomass, the world will be less dependent on fossil fuels and be contributing to a carbon dioxide neutral energy supply [10]. Among several alternatives reported in the literature, one may identify the exciting hydrogen production from steam reforming of vegetable oil, which comprises all referred striking consequences of biomass usage [see, for instance [3], and references therein].

Regarding the hydrogen storage issue, amid other solutions presented in the literature [11−17] the solid-state hydrogen storage using metal hydrides is an attractive strategy to overcome the limitations of gaseous and liquid alternatives [18,19]. Amidst all reversible hydrides for hydrogen storage, $MgH_2$ has the highest energy density (9 MJ/kg of Mg), along with high hydrogen gravimetric (7.6 wt %) and volumetric (6.5 H atoms. $cm^{-3}$) capacities. Besides, magnesium is a low-cost material and has a low specific weight, 1.45 g $cm^{-3}$, being the eighth most abundant element in the earth's crust [18].

The development of hydrogen storage materials, however, is currently impaired to two main different problems: (i) materials may have an appropriate hydrogen absorption/desorption temperatures near room conditions but with low storage capacity, and (ii) they may have high volumetric or gravimetric storage capacities but at very high desorption temperatures. In the case of magnesium, its practical application is linked with the last issue, i. e, the desorption temperature is in a range of 300−400 °C [19] with relatively low kinetics of hydrogen absorption/desorption [18].

Hydrides are not easily formed by merely exposing the metallic surface to hydrogen at RT, since there is usually a layer of oxide or hydroxide on the surface, preventing its direct contact with the gas. In the case of magnesium, the system must be heated at relatively elevated temperatures (at least 300 °C) to ensure fast reaction [20]. Two factors are responsible for this behavior. Firstly, the hydrogen gas must have access to the pure metallic magnesium to allow the reaction. As long as the magnesium oxide (or hydroxide) prevents such access, once the thermal expansion coefficients of the surface contaminants and the metal are different, the system must be heated to break this layer, thus exposing the metal to the hydrogen. Secondly, absorption kinetics is very slow at temperatures below 300 °C to generate hydrides within reasonable timescales [21].

It is well known that the formation of $MgH_2$ ceases after the establishment of a very thin layer of hydride on the metal surface [22]. This behavior has been correlated with a very slow (virtually none) diffusion of hydrogen through the hydride. Therefore, for the complete hydride formation, the starting metal must be of tiny geometric dimensions, i.e., either in particulate form, thin slices or films. Nevertheless, even with favorable geometric conditions, hydriding is supposed not to occur at RT because of the high activation energy for hydrogen gas dissociation. Exposure to oxygen only exacerbates the problem. Oxidized surfaces have higher activation energies for hydrogen gas dissociation than clean (activated) surfaces [23].

Lower desorption temperatures (<300 °C) has been reported for nanocrystalline $MgH_2$ obtained by ball milling [24], severe plastic deformation techniques (e.g., equal-channel angular pressing) [25−27], and through the addition of various catalysts [28]. Despite the advances produced by such techniques, especially in improving the desorption kinetics, temperatures of hydrogen desorption are considered still high, at least by the standards of the US DOE [29] which established as the ultimate goal a temperature range for hydrogen release from −40 to 85 °C.

Intermetallic compounds of transition metals are among several catalyst materials to assist the hydrogenation of the magnesium metal or destabilization of the magnesium hydride. In this case, the strategy of using composites is based on the mixture of dissimilar materials, exploiting the best characteristics of each component. It has been reported in the literature [30−32] the combination of TiFe, which absorbs and desorbs hydrogen at or near RT, with Mg, which has higher storage capacity than TiFe. HEBM has been used to produce the composites by mechanical alloying, usually starting from powders of Mg and TiFe in variable proportions. In these investigations, besides stoichiometric TiFe compound, $Ti_{1.2}Fe$ [30] and TiFeMn [31,32] powders were alternatively mixed with Mg powder. The best-reported result was achieved by Kondo et al. [32]. The authors have milled Mg and $TiFe_{0.92}Mn_{0.08}$ (50/50 wt%) in a planetary ball mill (Fritsch, Pulverisette 7), with some n-hexane, at 600 rpm for 80 h. After a lengthy heat treatment, the composite absorbed ~3.3 wt% of hydrogen at ~25 °C (1.55 MPa) for 20 h. Desorption started at 300 °C under a hydrogen pressure of 0.1 MPa.

In other studies, nanometric nickel [33] or multi-walled carbon nanotubes (MWCNTs) [34] were added to the $MgH_2$ + TiFe composites. The authors obtained good capacities (higher than 4.5 wt % of $H_2$) but at higher absorption/desorption temperatures (above 267 °C). Chen et al. [35] have also used CNTs but on Mg + 30 wt % TiFe composites. Astonishing capacity was obtained (6.6 wt %) at 150 °C after just 1 min. These results have emphasized the crucial role of a high dispersion grade of TiFe particles (nanoparticle dispersion) for the absorption/desorption properties and the necessity of activating the composite by heat treatment cycling.

In a previous work [36], we have performed HEBM of $MgH_2$+40 wt % TiFe using a planetary and a shaker mill. After dehydriding the as milled composites under vacuum at 350 °C, samples were cooled to perform kinetics measurements at RT. The best hydrogen kinetics (3 wt % at the first hour) was attained by the composite sample prepared in the planetary mill for 36 h. Higher hydrogen capacity (4.0 wt %) was observed - for the specimen milled in the shaker mill for 2 h - but only after 13 h of exposure to hydrogen.