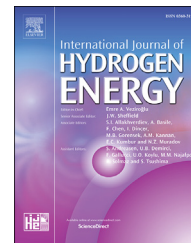


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Effect of additive distribution in H₂ absorption and desorption kinetics in MgH₂ milled with NbH_{0.9} or NbF₅

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ABSTRACT

This paper presents a comparative study of H₂ absorption and desorption in MgH₂ milled with NbF₅ or NbH_{0.9}. The addition of NbF₅ or NbH_{0.9} greatly improves hydriding and dehydriding kinetics. After 80 h of milling the mixture of MgH₂ with 7 mol.% of NbF₅ absorbs 60% of its hydrogen capacity at 250 °C in 30 s, whereas the mixture with 7 mol.% of NbH_{0.9} takes up 48%, and MgH₂ milled without additive only absorbs 2%. At the same temperature, hydrogen desorption in the mixture with NbF₅ finishes in 10 min, whereas the mixture with NbH_{0.9} only desorbs 50% of its hydrogen content, and MgH₂ without additive practically does not releases hydrogen. The kinetic improvement is attributed to NbH_{0.9}, a phase observed in the hydrogen cycled MgH₂ + NbF₅ and MgH₂ + NbH_{0.9} materials, either hydrided or dehydrided. The better kinetic performance of the NbF₅-added material is attributed to the combination of smaller size and enhanced distribution of NbH_{0.9} with more favorable microstructural characteristics. The addition of NbF₅ also produces the formation of Mg(H_xF_{1-x})₂ solid solutions that limit the practically achievable hydrogen storage capacity of the material. These undesired effects are discussed.

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Introduction

MgH₂ continues to be one of the most promising materials for hydrogen storage due to its high capacity (7.6 wt%), low cost, environmental friendliness and ubiquity (one of the most important Mg reservoirs is sea water). Besides, it has good

reversibility during successive cycles of hydrogen absorption and desorption. This is why there is still much research being done to overcome its main drawbacks: its low desorption pressure at operative temperatures and its slow kinetics.

Regarding kinetics, many advances have been achieved by the use of ball milling. This technique, which comminutes MgH₂ particles, reduces crystallite size, and generates defects

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and strain, considerably improves hydrogen absorption and desorption kinetics [1]. An extra benefit is obtained through the use of additives [2]. In particular, Nb-based additives like NbH_x ($x < 1$), Nb and NbF_5 have shown promising results [3–22]. In the case of MgH_2 milled with NbH_x , a physical mixture is formed where morphological and structural properties of both compounds are refined yielding kinetic improvements. For example, Zhang et al. [3] have compared hydrogen sorption kinetics in MgH_2 milled with three kinds of NbH_x -nanoparticles synthesized by wet-chemical methods, and have observed that the better performance is obtained with the additive with more disordered structure and/or smaller particle sizes. Song et al. [4] have studied the behavior of MgH_2 milled with NbH_x obtained by hydriding commercial Nb, and have reported an improvement in hydrogen absorption and desorption kinetics, and a significant decrease in thermal desorption temperature. Regarding Nb as additive, it has been incorporated to MgH_2 or Mg by milling [5–9], by sputtering [10,11] or by hydrogen plasma metal reaction (HPMR) [12]. Huot et al. [5,6] have studied 20 h-ball-milled $\text{MgH}_2 + 5$ at.% Nb and have achieved complete hydrogen desorption in 5 min at 573 K. They have also reported the formation of a metastable NbH_x ($x \approx 0.6$) phase during hydrogen desorption that they suggest could act as a hydrogen gateway. In addition, Pelletier et al. [13] and Kim et al. [14] have suggested that this metastable NbH_x would prevent Mg/ MgH_2 coalescence. de Castro et al. [7] have studied the behavior of Mg–Nb nanocomposites processed by reactive milling and have reported a decrease in the thermal desorption temperature of the nanocomposites. For a similar content of Nb, a moderate improvement has been reported by Gasan et al. [8] after only 2 h of milling. Interestingly, core-shell like nanostructures have been prepared by milling and mixing Mg/ MgH_2 and NbCl_5 in THF by Cui et al. [9]. These materials have presented very good kinetic performance with an important decrease in thermal desorption temperature and considerable dehydriding even at 225 °C. Additionally, Nb nanoclusters and nanoparticles have also shown significant catalytic properties in Mg–Nb films and nanocomposites [10–12]. Concerning NbF_5 , Luo et al. [15] have reported better hydrogen sorption kinetics in a mechanically milled $\text{MgH}_2 + 2$ mol.% NbF_5 mixture compared with a $\text{MgH}_2 + 2$ mol.% Nb + 5 mol.% MgF_2 material synthesized under the same conditions. Jin et al. [16,17] have shown very promising results in isothermal absorption kinetics and non-isothermal desorption, with remarkable good behavior of NbF_5 among several transition-metal fluorides. Recham et al. [18] have reported that the addition of NbF_5 produces better hydrogen sorption kinetic behavior than the use of NbCl_5 or Nb_2O_5 . And Malka et al. [19,20] have studied the effect on hydrogen sorption kinetics of adding different halides to MgH_2 and have reported an excellent performance of NbF_5 over all the studied compounds, only overcome by ZrF_4 . Finally, Floriano et al. [21] have shown by DSC and volumetric experiments that the addition of NbF_5 to MgH_2 results in better hydrogen absorption and desorption kinetics than the incorporation of Nb_2O_5 or Nb.

It has been reported that when NbF_5 and MgH_2 are milled together, they react producing NbH_x and MgF_2 [16]. However, further studies using greater NbF_5 amounts have shown that a solid solution $\text{Mg}(\text{H}_{0.8}\text{F}_{0.2})_2$ with H^- partially substituted by F^-

is formed [22]. The effect on hydrogen sorption kinetics of these compounds is not clear yet [23–27]. According to some reports, MgF_2 is not beneficial for hydrogen absorption and desorption. For example, Leiva et al. [23] have observed that the onset desorption temperature is slightly higher in MgH_2 obtained by milling Mg + MgF_2 under H_2 than in MgH_2 obtained by milling pure Mg. Similarly, Ma et al. [24] have reported that MgH_2 and $\text{MgH}_2 + 6$ mol.% MgF_2 have comparable absorption and desorption properties. More recently, Tortoza et al. [25] have presented a study of the Mg–H–F system and have shown that hydrogen take up and release in $\text{Mg}(\text{H}_x\text{F}_{1-x})_2$ solutions have slower kinetics than in MgH_2 . On the contrary, Jain et al. [26] have shown that $\text{MgH}_2 + \text{MgF}_2$ presents better hydriding and dehydriding kinetics than MgH_2 without additive. And, in a different system ($\text{MgH}_2 + \text{TiF}_3$), Mulder et al. have proposed that MgF_2 could enhance hydrogen absorption by acting as a nucleation center for MgH_2 [27].

From this literature survey it is clear that the addition of Nb or Nb-based compounds has a substantial effect on hydrogen absorption and desorption kinetics. However, it is interesting to note that the comparison of the effect of different Nb compounds added to MgH_2 in identical proportion following the same experimental procedure has only been made in a few cases [15,21]. In particular, to the best of our knowledge, there are no reports that compare the effects of NbF_5 and NbH. Additionally, there is still disagreement on the effect of MgF_2 on hydrogen sorption kinetics [23–27]. Taking all this into account, we present here the study of hydrogen absorption and desorption behavior of two systems obtained by mechanical milling: $\text{MgH}_2 + \text{NbH}_{0.9}$ and $\text{MgH}_2 + \text{NbF}_5$. By comparing these materials we identify that $\text{NbH}_{0.9}$ is the phase that produces the kinetic improvement, and establish some differences among the $\text{NbH}_{0.9}$ incorporated as additive and that produced from the reaction between NbF_5 and MgH_2 . These differences correlate with the kinetic performance of the materials. Additionally, we discuss the effects of $\text{Mg}(\text{H}_x\text{F}_{1-x})_2$ solid solutions that form instead of MgF_2 during milling. In particular, we analyze their effect on hydrogen sorption and the limitations they impose for hydrogen storage.

Materials and methods

The materials were prepared using commercial MgH_2 (Sigma Aldrich, 96.5%, particle sizes in the 10–100 μm range), NbF_5 (Sigma Aldrich, 98%), and lab-made $\text{NbH}_{0.9}$. The Nb hydride was obtained by hydriding small pieces of Nb (Alfa Aesar, 99.95%) at 450 °C and subsequently milling under 5 bar H_2 at room temperature. The Rietveld refinement of the diffractogram confirms that all the peaks correspond to the orthorhombic β - $\text{NbH}_{0.9}$ phase (the composition was determined by interpolating composition vs. cell volume data available in the literature [28–31]). Mixtures of $\text{MgH}_2 + 7$ mol.% $\text{NbH}_{0.9}$ were milled in a low energy milling device (Uni-Ball-Mill II, Australian Scientific Instruments) for 10 and 80 h with a ball-to-powder mass ratio equal to 50:1 under Ar atmosphere. These materials are labeled MN10 and MN80, respectively. Additionally, a $\text{MgH}_2 + 7$ mol.% NbF_5 mixture was milled under the same conditions of MN80. This material is labeled MNF80. As a reference, commercial MgH_2 was milled under identical conditions (labeled M80).

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