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Catalytic effect of additives on the hydrogen absorption properties of nano-crystalline $MgH_2(X)$ composites

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Abstract

Hydrogen sorption properties of MgH_2–X nanocomposite powders (X=V, Nb, Ti, TiCN) are conditioned by the milling step. The respective roles of the additives and the milling time have been dissociated. The study reveals details not only on the hydrogen sorption process but also on the particle size reduction, distribution and agglomeration, that depend on the nature of the additives. In addition to the effect related to the extra-elements, the milling time has to be optimised to lead to the best particles size reduction without any agglomeration of the grains.

Keywords: Magnesium hydride; Activation procedure; Ball milling

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1. Introduction

Regarding the use of hydrogen in fuel cell for transport applications, metal hydrides can offer a high hydrogen volume capacity and a safe alternative compared with liquid storage or with compressed gas up to 50 MPa. Among the metal hydrides to consider, magnesium has a theoretically high weight capacity for H-storage, a reasonably low cost thus it appears promising for mobile applications. Recently, relevant and competitive sorption properties have been achieved with the preparation of nano-crystalline magnesium hydrides using high energy ball milling [1,2]. Presently, many studies are devoted to the catalytic effect on hydrogen sorption of metals [3,4] or metal oxides [5] added to MgH_2 or Mg powder during ball milling. But up to now, the mechanism involved when using these additives was not clearly established regarding to their efficiency at a microscopic scale.

This study is then a contribution to highlight the general influence of the two main parameters involved when catalysing hydrogen sorption in nano-crystalline milled MgH_2 powders: the additives and the ball milling conditions. Even if these two parameters are strongly correlated during sample preparation and have combined effects on hydrogen storage and kinetics properties [6], we aimed to dissociate both influences through kinetics results and microscopic observations. The results are discussed here towards the role of each parameter.

2. Experimental procedure

Pure MgH_2 powder (from Th. Goldschmidt AG, 95% MgH_2, 5% Mg) was mixed with 5 at.% niobium, vanadium and titanium for kinetics studies and with 5 at.% TiCN for microscopic studies. Hardened steel crucibles of 10 cm in diameter and containing six balls were filled and locked under argon with a ball to powder weight ratio of 10:1. The Fritsch Pulverisette 5 was used with a rotation speed of 360 turns per min and with the various milling times of 20, 100 or 200 h. The hydrogen storage properties of MgH_2 powders mixed with Nb, V and Ti were evaluated with a home made thermogravimetry balance. The kinetics curves at various temperatures were recorded after a few cycles. The microstructural characterisation of pure MgH_2 powders and when mixed with Ti and TiCN were done by

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using both scanning electron microscopy (SEM) and a Coulter Particle Size Analyser.

3. Results and discussion

The influence of additives to MgH_2 nano-crystalline powder on hydrogen absorption kinetics depends on temperature. Fig. 1 gives a comparison between the hydrogen absorption curves recorded at various temperatures, under 1 MPa of hydrogen and after 100 h milling, for a pure MgH_2 powder and for a MgH_2+5 at.% vanadium powder. At low temperatures (below 523 K), the effect of vanadium is marked with a high slope during the first minutes. Whereas, a pure MgH_2 powder absorbs hydrogen very slowly and no further absorption can be activated below 423 K. At 603 K, both absorption kinetics (with and without vanadium) are very similar. The pure MgH_2 powder reaches a higher absorption rate because no additives are included to account of the mass sample. For the MgH_2+5 at.% vanadium powder, kinetics is even lower at 603 K than at 523 K: the vanadium is no more efficient to activate hydrogen absorption, because the δ-VH_x hydride is no longer stable. We conclude that, below 573 K, additives lead to suitable kinetics. Whereas, at 603 K, faster kinetics results from the grain size reduction during ball milling since the kinetics found are significantly high even for pure MgH_2 nano-crystalline powder when fine enough. This enables to distinguish between two behaviours exhibiting differences with thermal conditions and to dissociate the effect of metal additives from that of the milling conditions.

To go further into the role of additives only, absorption kinetics curves have been compared for three MgH_2 powders milled under the same conditions (100 h) and mixed with three different additives (V, Nb and Ti) (Fig. 2). At 423 K, hydrogen absorption is not activated for the MgH_2+5 at.% Ti powder but is the fastest for MgH_2+5 at.% Nb. The slopes of the two curves for MgH_2+5 at.% Nb and MgH_2+5 at.% V are quite different at the very beginning of absorption but within 12 min, nearly 3% of hydrogen is absorbed in both cases. At 553 K, the initial slope is sharp for MgH_2+5 at.% V and MgH_2+5 at.% Nb and a two-regime behaviour is observed. Absorption rates of 4 and 4.5% are obtained for respectively, MgH_2+5 at.% Nb and MgH_2+5 at.% V in less than 2 min. Above this uptake level, the kinetics is found very low. For MgH_2+5 at.% Ti, the slope is lower at the beginning of the reaction but the absorption mass is the highest (6%) after 12 min reaction. As shown here, the addition of pure elements on samples prepared in the same milling conditions reveals marked differences depending on the nature of the added metal. Here titanium does not exhibit high activation effect. This appears to be in contrast with the results of Ref. [3]. Concerning the direct influence of extra metal particles, the affinity of these added elements towards hydrogen should be the first parameter to consider. Hydrogenation of the extra metal particles favours hydrogen diffusion into the Mg particle if ever the microstructure of the composite is optimised. Then the absorption process is found to mainly depend on temperature and pressure conditions, in agreement with the differences observed between the addition of Nb and V. A second parameter to consider is the quality of the nano-structure, that must be questioned, particularly in the case of the present titanium doped material.

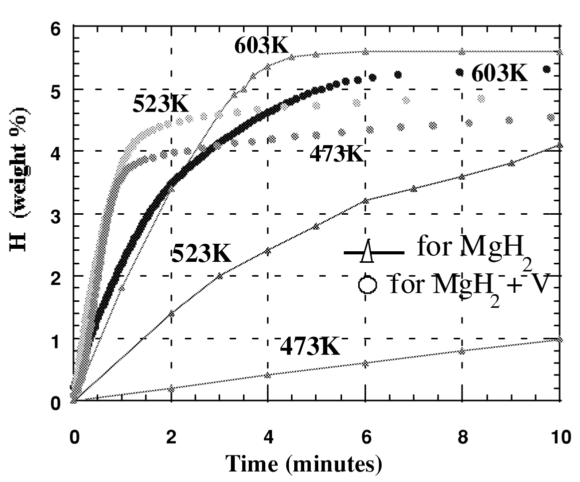


Fig. 1. Comparative absorption kinetics at various temperatures for pure MgH_2 powder and MgH_2+5 at.% V powder after 100 h milling time.

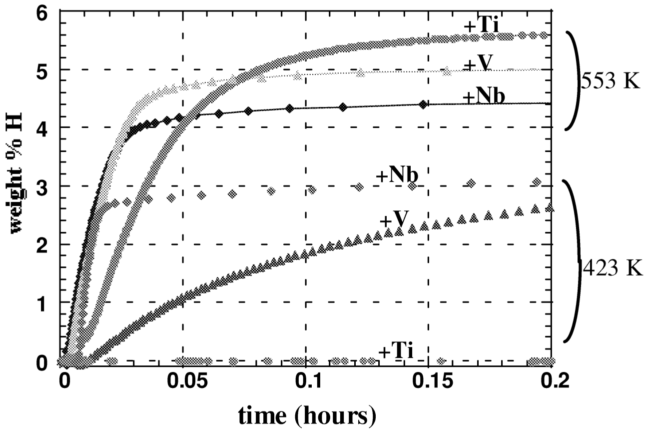


Fig. 2. Comparative absorption kinetics at 423 and 553 K and after 100 h milling time for MgH_2 powder mixed with 5 at.% Ti, 5 at.% V and 5 at.% Nb.

Other parameters can also influence the hydrogen absorption and among them, the ability of the added element to:

- Finely disperse and realise a close and homogenous mixing onto the Mg particles.
- Establish physical or chemical bonds with Mg, i.e. truly alloyed surface.

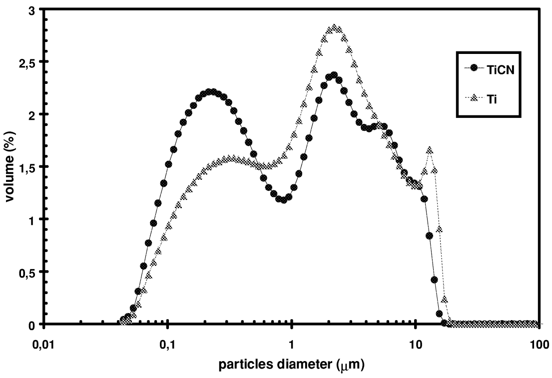
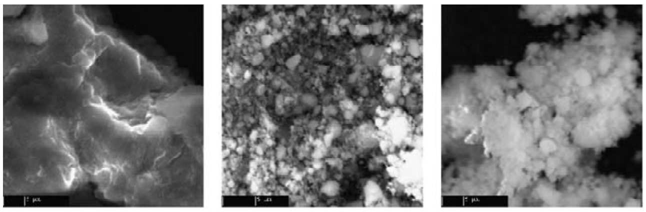


Fig. 3. Comparative particle size distributions for MgH_2+5 at.% Ti and MgH_2+5 at.% TiCN after 100 h milling time.



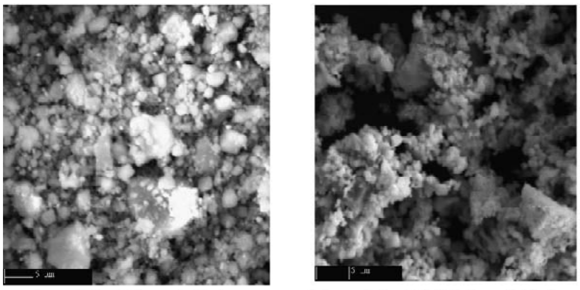
a) 0 hour b) 100 hours c)200 hours

Fig. 5. SEM images of the pure MgH_2 powder after different milling times (scale-is 5 μm).

Optimise the surface to volume ratio of the embedded Mg particle to favour large hydrogen interaction.

For this, a mechanical grinding effect of the added metal is required in order to reduce the Mg particle size. So, the hardness of the extra element is the key factor [7]. To test the relevance of such a grinding effect, the particles size distribution has been compared for MgH_2+5 at.% Ti and MgH_2+5 at.% TiCN both milled for 100 h. These two additives may reveal similar chemical behaviour towards Mg but have quite different hardness (970 HV for Ti and 2300 HV for TiCN). Fig. 3 shows an increase in the amount of the smallest particles (size near 0.2 μm) with a corresponding decrease in the amount of coarser particles (>1 μm) when the hardness of the element increases. Moreover, SEM pictures (Fig. 4) show different microstructures for the two types of composites. In the case of Ti addition, the mixture is rather homogeneous with few agglomerates. The Ti initial particles (in white on Fig. 4a) are still present with a reduced grain size (50 μm before milling) but with a rather bad coating of the Mg particles. This clearly shows the poor efficiency of milling magnesium with titanium. For TiCN addition, the microstructure is found finer but agglomeration is more effective and it leaves some coarse even intact MgH_2 particles. The initial TiCN particles (in white on Fig. 4b) are also reduced in size (from 7 μm before milling to less than 1 μm). However, no absorption could be activated yet on the MgH_2+5 at.% TiCN powder. TiCN is very stable towards hydrogen and the catalytic conditions on hydrogen absorption were not realised. This shows that, on the one hand, hard additives can drastically reduce the MgH_2 grain size during milling but on the other hand the de-agglomeration efficiency as well as the reactivity of the extra elements towards hydrogen prevails on the final absorption properties.

To complete these results, the influence of pure milling (without additives) has been analysed in terms of the MgH_2 microstructure. On Fig. 6, the average particles size as observed using SEM (Fig. 5) is plotted vs. the milling time. Fig. 6 shows a drastic size reduction in the particles size when increasing the milling time up to 100 h. After 200 h of milling time, the particle size remains nearly unchanged, whereas agglomeration seems to prevail in this case, as shown in Fig. 5c. Moreover, the particle size distribution was analysed on a 100 h milled MgH_2 powder vs. the ultrasonic de-agglomeration time (Fig. 7). Increasing the time of the ultrasonic treatment leads to an increased number of particles near 0.5 μm. This is to correlate with a first decrease in the number of agglomerates sized above 10 μm and a subsequent decrease of agglomerates sized above 1 μm for longer ultrasonic



a) with Ti addition b) with TiCN addition

Fig. 4. SEM images of the MgH_2 powders after 100 h milling time with respectively, (a) 5 at.% Ti addition; and (b) 5 at.% TiCN addition (scale-is 5 μm).

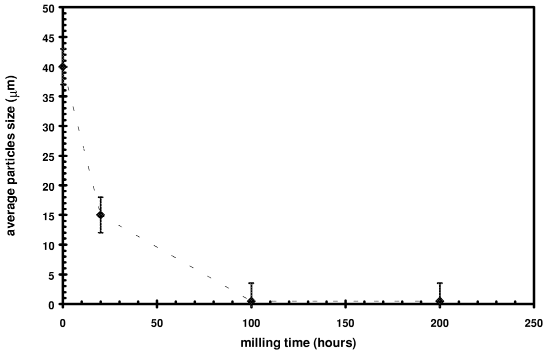


Fig. 6. Average particles size of pure MgH_2 powders vs. the milling time.

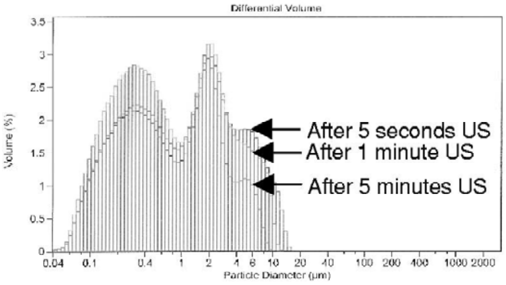


Fig. 7. Comparative particles size distributions measured on pure MgH_2 powders after 100 h milling time and after three different times of de-agglomeration by ultrasonic treatment.

applied treatments. These results should be completed soon by a kinetics study. Presently, we can conclude that for a pure MgH_2 powder, size reduction is needed for better reactivity but milling times longer than 100 h are rather detrimental to hydrogen absorption properties due to the marked agglomeration effects. In terms of the final hydrogenation properties herein discussed, the agglomeration aspect of the nano-crystalline powder appears as important as the particle size itself.

4. Conclusion

Hydrogen absorption properties of MgH_2 powders are strongly conditioned by the milling step. They depend on the nature and properties of the metal additives not only for the hydrogen absorption process but also in terms of the particle size reduction and distribution and finally of the particles agglomeration efficiency.

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