

Article

Microstructural and Kinetic Evolution of Fe Doped MgH_2 during H_2 Cycling

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Abstract: The effect of extended H_2 sorption cycles on the structure and on the hydrogen storage performances of MgH_2 powders with 5 wt% of Fe particle catalyst is reported. MgH_2 powders with and without Fe have been ball milled under Argon, the doped MgH_2 nanocomposite has been cycled under hydrogen pressure up to a maximum of 47 desorption and absorption cycles at 300 °C. After acceleration during the first 10 cycles, the kinetics behavior of doped MgH_2 is constant after extended cycling, in terms of maximum storage capacity and rate of sorption. The major effect of cycling on particle morphology is the progressive extraction of Mg from the MgO shell surrounding the powder particles. The Mg extraction from the MgO shell leaves the catalyst particles inside the hydride particles. Many empty MgO shells are observed in the pure ball milled MgH_2 upon cycling at higher temperature, suggesting that this enhancement of the extraction efficiency is related to the higher operating temperature which favors Mg diffusivity with respect to the H ion one.

Keywords: hydrogen storage; MgH_2 ; cycling; magnesium; nanocomposites; ball milling; scanning electron microscopy (SEM)

1. Introduction

Hydrogen is often considered an important energy carrier for a carbon-free management of the energy. Among the principal problems in the development of the necessary technological framework, the storage of hydrogen, in a safe and economical way, represents a critical issue.

Besides compressed and liquefied hydrogen, metal hydrides and complex hydrides can be used for storage in the solid state, with good performances in terms of safety and storage capacity. For this reason, the reaction of hydrogen with some selected metal and complex compounds to form hydrides is the object of in depth investigations. Both the hydride formation, with the solid state stabilization of the hydrogen within the solid state, and the hydride decomposition, providing back H_2 gas, are of interest in this regard, being related to the tank refueling and to the fuel delivery, respectively.

In particular, the Mg/MgH₂ system is attractive due to a high theoretical gravimetric capacity, to the reversibility of the reaction with hydrogen and to the relatively low cost of the base material [1]. Moreover, in contrast to some intermetallic compounds, which show significant degradation against cycling [2], the binary metal hydride systems exhibit good resistance against repeated desorption-absorption phase transformations [3,4]. On the other hand, these sorption reactions are quite slow so that high temperatures are required for fast hydrogen absorption and release. The reaction speed is further deteriorated by the surface contamination owing to the magnesium reactivity with air and moisture. Even if presently the performances in terms of sorption rate are still far from the targets for technological applications (DOE, Department of Energy, Washington DC, USA) [5], the reactions of Mg with H_2 have been significantly accelerated by nanostructuring the material generally performed by ball milling with catalyst addition. In fact, the introduction of defects, the refinement of particle size and the presence of catalyst particles play an important role in reducing the working temperature and in speeding up the reaction rate with H_2 [6,7].

Hydride formation and decomposition are influenced by the sample microstructure. The average powder particle size, the nature and the amount of the employed catalyst, together with the presence of surface contamination have been shown to affect the reaction kinetics in terms of mechanisms limiting the reaction rate.

In the last decades the catalytic effect of most 3d-transition metals [8,9] and of most of their oxides [10,11] has been experimented to be effective for the purpose of speeding up the rate of the hydrogen sorption reactions with a lowering of sorption temperature. Also intermetallic compounds such as Zr_xNi_y are emerging as promising catalysts for MgH₂ [12].

Among 3d-transition metals, Fe as catalyst has shown competitive performances for technological application [13,14]. A further advantage in its utilization is its low cost and high availability.

The reaction kinetics is usually studied by fitting the reaction rate to specific kinetics models with the purpose of obtaining information on the reaction rate-limiting step and on the kinetics parameters. The Johnson-Mehl-Avrami (JMA) model is commonly applied to the isothermal solid state reactions [15–17]. It has also been demonstrated that by supporting this kind of kinetics analysis with a high resolution metallographic examination of the material, able to provide the spatial distribution of the present phases, can result in a better and more realistic definition of the reaction path and of the reaction rate limiting step [18,19].

In this paper we report on the structural modifications imparted to Mg powder particles by a sequence of hydrogen absorption and desorption reaction. Despite a few works describing kinetics and microstructural modifications upon cycling [20,21], very little is known on the performances of materials submitted to a large number of H₂ charging and discharging; furthermore also the detailed evolution of the sample microstructure is largely missing.

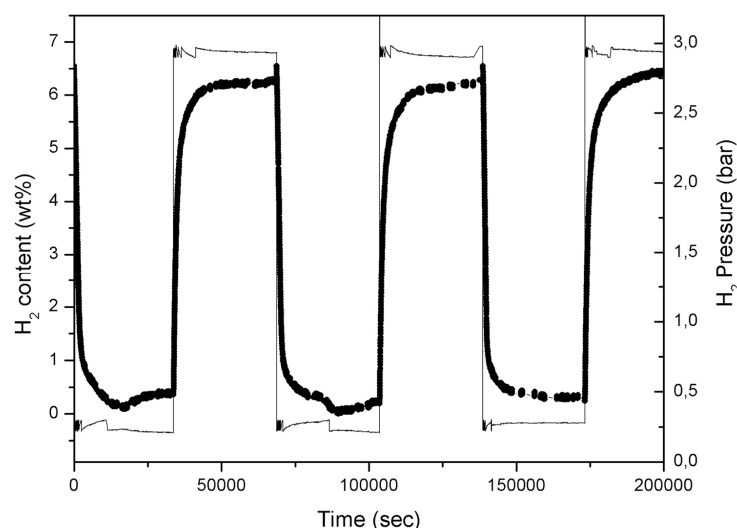
Indeed, major microstructural modification and change in the sorption properties are expected as a consequence of the long time exposure to relatively high temperature and of the noticeable volume expansion of the order of 30% occurring during phase transformation between Mg and MgH₂. The purpose is to report experimental results relative to the modifications of the microstructure and of the reaction kinetics upon cycling both catalyzed with 5 wt% of Fe and pure Mg powders with hydrogen. The performance of the material was characterized, up to a maximum of 47 cycles, by the maximum hydrogen storage capacity and by the reaction speed, whose parameters are derived by the analysis of the reaction rates. The microstructure of the samples during H₂ cycling was studied by Scanning Electron Microscopy, both on powders and on cross sectional samples exposing the material bulk.

2. Results and Discussion

2.1. Results

A portion of the full cycling experiment carried out on Fe-doped MgH₂ is shown in Figure 1 where a typical plot reporting the hydrogen content in Mg *versus* time is reported.

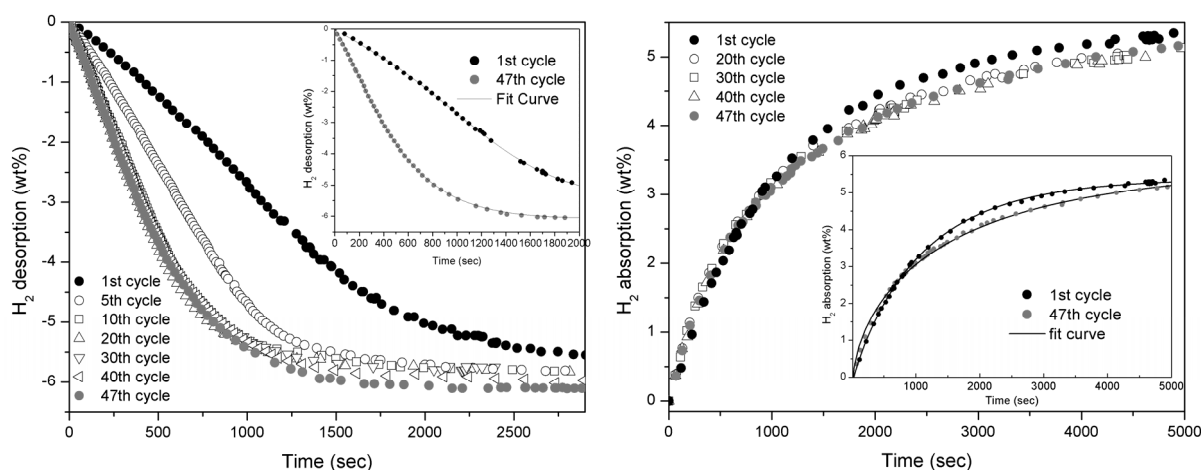
Figure 1. H₂ desorption and absorption curve of three cycles for 5% Fe-doped MgH₂ powder: scatter line; hydrogen pressure profile is also superimposed: full line.



In Figure 1 the in-chamber H₂ pressure is also reported in order to illustrate the operating procedure. Changing periodically the H₂ pressure between 3.0 and 0.2 bars induces an alternate phase transformation between Mg and MgH₂. The temperature profile (data here not reported) evidences a practically constant temperature with negligible thermal fluctuation during the cycling time.

The absorption and desorption curves concerning doped MgH_2 are reported in Figure 2. In desorption, kinetics undertake a small improvement in the firsts ten cycles and then maintain the same kinetic for the rest of cycling (Figure 2a). In absorption, indeed, the performances are about constant all along the cycling apart from a slight worsening of the kinetic as it is shown in the inset of Figure 2 b.

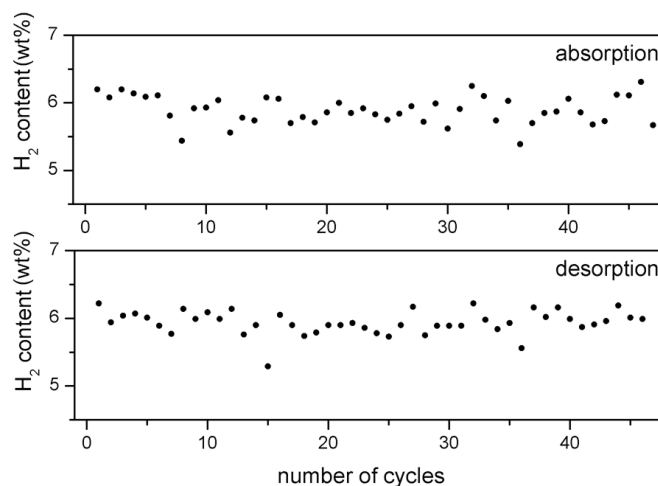
Figure 2. Desorption (**left**) and absorption (**right**) curves of MgH_2 doped with 5 wt.% of Fe taken at 300 °C and 0.2 bar for desorption and 10 bar for absorption.



The Johnson-Mehl-Avrami (JMA) model applied on these curves satisfactory fits the experimental data concerning all the hydrogen absorption and desorption curves. Avrami exponent n values shows a reduction by increasing the number of cycles, both for the absorption and the desorption reactions. In the former case we observe a reduction from ≈ 1 to ≈ 0.5 while in the latter from ≈ 1.7 to ≈ 1.2 . These changes in the kinetic parameters indicate that repeated cycling induces major modifications of the sample structure, affecting the reaction path and the rate-limiting step.

Despite this effect, the hydrogen storage capacity of about 6 wt% remains largely unaffected (Figure 3).

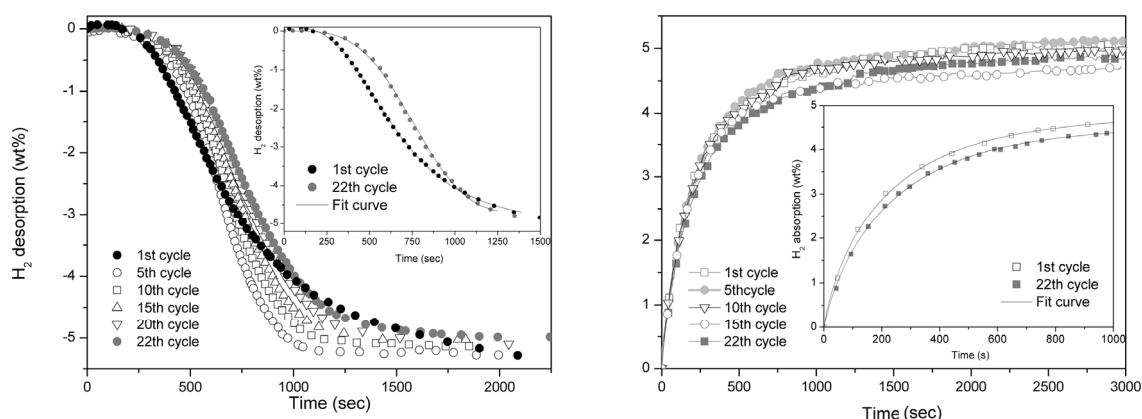
Figure 3. H_2 storage capacity of 5 wt% Fe-doped MgH_2 after each absorption and desorption cycle versus number of cycles.



As reference, pure MgH_2 kinetics is reported in Figure 4. In this case the reaction is much slower, in fact, to have a comparable reaction time, the isothermal cycling was performed at 350 °C. In both desorption and absorption reactions, the absence of catalyst implies a gradual degradation of reaction rate even if slightly evident in the former one. The Avrami exponent, n , for desorption reaction evolves from a value of 4 observed at first cycle to about 3.5 after 22 cycles. In the case of H_2 absorption, n is 0.8 and does not show any evolution upon cycling. The hydrogen storage capacity remains unaffected also in MgH_2 sample after 22 cycles.

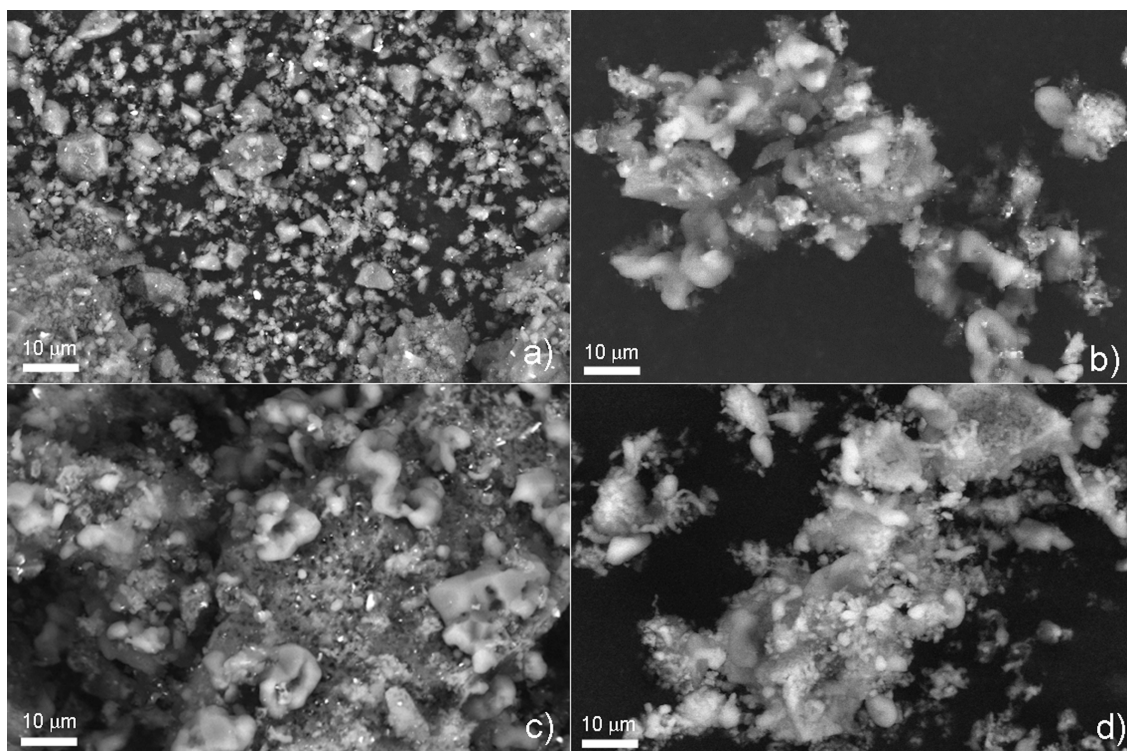
From the comparison of the curve fitting between Fe- MgH_2 and pure MgH_2 , the rate-limiting step of the absorption reaction is controlled by the same mechanism. The value of n in the range from 0.5 to 1 suggests a transformation at constant density of MgH_2 nuclei and controlled by limited hydrogen flux at the powder particle surface [22]. In the case of desorption reaction, the process is influenced by the presence of Fe. In fact, in the case of pure MgH_2 the reaction is interface-controlled with a three-dimensional growth at constant nucleation rate while, in the case of Fe- MgH_2 , the desorption reaction is diffusion-controlled.

Figure 4. Desorption (left) and absorption (right) curves of pure MgH_2 taken at 350 °C and 0.2 bar for desorption and 10 bar for absorption.



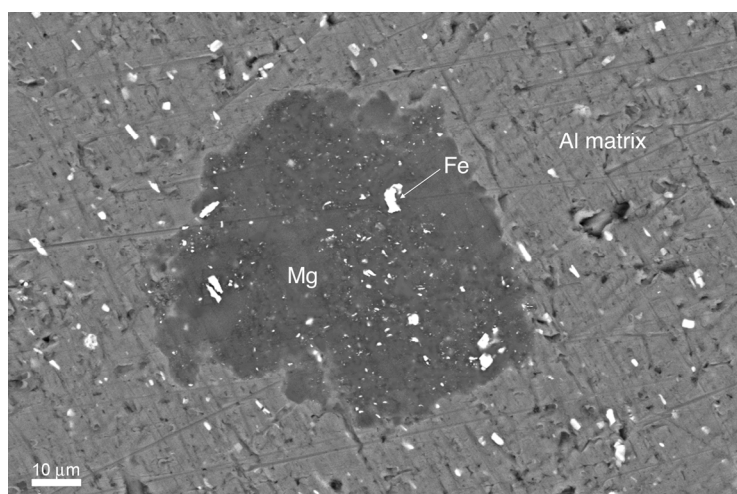
SEM observations confirm that major modifications of sample microstructure occur during the cycling experiment. Backscattered electron (BSE) images of MgH_2 with 5 wt% of Fe at different number of cycling (Figure 5a–c) clearly show the localization of the catalyst particles visible as white dots. From the morphologic point of view, upon cycling the material evolves from a typical structure of as milled powder, characterized by irregular shape and broad particle size distribution function and still maintained after the first cycle [23] (Figure 5a), to a powder constituted by larger agglomerates, where surface protrusions can be observed (Figure 5b,c). After several cycling, the internal material appears to come out from the particle surface, giving rise to worm-like structures where no catalyst particles are present. Similar microstructural evolution is observed for as milled [22] and cycled pure MgH_2 powder (Figure 5d). In particular the extent of protrusion is comparable to the catalyzed sample with the same number of cycles as well as the size of the agglomerates.

Figure 5. SEM-BSE images of 5 wt% Fe-doped MgH_2 , ball milled for 10 h, after (a) 1 cycle; (b) 22 cycles and (c) 47 cycles at 300 °C; (d) SEM-BSE images of pure MgH_2 , ball milled for 10 h after 22 cycles, at 350 °C.



Besides particle coalescence, which can be expected considering the relatively high processing temperature, some other important effect seems to be directly related to the H_2 cycling. This hypothesis is confirmed by the observations of the internal structure reported in Figure 6.

Figure 6. SEM-BSE image of 5 wt% Fe-doped MgH_2 , ball milled for 10 h, after 47 cycles (cross section). The white spot.



As it is possible to noticing in Figure 6, the particle structure is assuming a core shell configuration with the catalyst particles concentrated in the core structure and an outer shell where only Mg without Fe particles is observed.

A similar evolution can be found in the images reported by Malka *et al.* [24] in an analogous experiment.

Another important effect related to the H_2 cycling, besides the particle coarsening, is observed in the morphology of pure MgH_2 after 22 cycles in Figure 7. Also in this case Mg appears to exit from the MgO crust surrounding the particles. This effect is particularly evident in the smaller particles where partially empty structures can be seen in the higher magnification Secondary Electron (SE) image.

Figure 7. SEM-SE image of pure MgH_2 after 22 cycles.



2.2. Discussion

The repeated phase transformation between the MgH_2 and Mg induces major modifications to the powder material. Concerning the catalyzed sample, both the structure and the mechanisms underlying the hydrogen absorption and release appear strongly modified by this processing.

The main morphological and structural effect is constituted, besides a noticeable coarsening of the powder structure, by the presence of the material, which protrudes out of the powder particles and which is constituted by only pure Mg without the catalyst particles.

Morphological details of ball milled powder particles involved in the reaction with hydrogen gas can provide a tentative explanation for this effect. It is known from literature [25] that the powder particles have a core-shell structure with a metallic core surrounded by a surface layer, in the nm range thickness, constituted by Mg oxide or hydroxide, resulting from the exposure of the just milled material to the atmosphere. When the Mg based particles react with hydrogen to form the MgH_2 phase, this layer separates the two reacting species so that, in order for the reaction to occur, one or both elements have to diffuse through this MgO membrane. It is quite evident that the amount of the product phase formed on either side of the membrane is related to the diffusion fluxes of the reacting elements. This means that the product phase will be located on a single face of the MgO membrane only if the diffusive flux of one of the reactants through this separation layer is negligible with respect to the other. In a simplified example, if hydrogen is the only mobile specie in the MgO layer, the product phase is expected to be synthesized inside the particle while in the opposite case, if only Mg is mobile, MgH_2 is expected to form outside the particle. In a general case, if both the diffusive fluxes are of the same order of magnitude, the product phase will be formed on either side of the membrane in a fraction inversely proportional to the diffusivity of the elements present on that side at the beginning of the reaction. The driving force for diffusion process is provided by the difference in the Gibbs free

energy between the reacting elements and the product phase, which generates a chemical potential gradient across the surface membrane for both the reacting species [26].

During the inverse reaction, hydrogen is released by the decomposition of the MgH_2 . Considering that MgH_2 can be located either inside the MgO shell surrounding the particles or outside, the hydrogen released in the former case has to cross the MgO layer while this step is not necessary in the latter case. In the former case the driving force inducing the diffusive flux through the membrane is provided by the difference between the internal pressure, which can be considered of the order of the equilibrium pressure at the operating temperature and the external pressure which is kept at a lower value in order to induce the hydride decomposition. It is important to notice that this scenario provides a driving force only for hydrogen diffusion and no driving force is present to assist Mg mobility. In particular there is not any driving force forcing the Mg atoms backward inside the powder particle, so that the net result of a full charge-discharge cycle is that a fraction of the Mg atoms are extracted from the MgO shell. Considering that this effect is operative during each cycle, the fraction of Mg present outside the original powder grains is expected to increase with the number of cycles.

Due to the catalytic activity, Fe does not react with hydrogen but assists the phase transformation and, as a consequence, is expected to remain trapped inside the MgO crust as noticed in Figures 5 and 6.

Most of the experimental observations reported in this paper can be accounted for by the delineated hypothesis. In fact the Mg is observed to protrude out of the powder particles only at localized sites where, probably the structure of the MgO layer is supporting a particularly fast diffusion of Mg atoms. The Fe catalyst particle are not observed to participate in the process and are observed to concentrate, in many cases, in a defined volume of the material leaving space for areas where only pure Mg is observed. These findings are supported by the experimental results concerning the cycling of pure Mg . In this case the cycling temperature has to be increased to $350\text{ }^\circ\text{C}$ in order to compensate for a lower reactivity of the sample. The experimental result reported in Figure 7, where many empty MgO shells can be observed, confirms that also in this case Mg is extracted from the MgO shell by the hydrogen cycling process. Moreover, in this case, the process appears to be more efficient since particles completely free of the Mg core are observed after only 22 cycles; this enhancement of the extraction efficiency can be related to the higher operating temperature which can favor Mg diffusivity with respect to the H ion one.

The experimental results reported in this paper can have important practical applications. In fact the process can be interpreted as an *in situ* cleaning of Mg which, after cycling, can be present in a hydrogen tank without the MgO crust since the process is carried out completely under an hydrogen atmosphere and the fresh Mg surface can be stable in this environment. We want to notice that, within the sensitivity of our methods no further MgO is formed during cycling, since the total hydrogen storage capacity of the material remains constant. Considering that the surface reactivity of Mg has been often considered as an important drawback for technological application in the hydrogen storage, our observation can open new routes for producing tank devices filled with clean Mg base material.

However, these observations highlight quite complex phenomena, which require a deeper investigation for a full explanation. In fact, even if the progressive extraction of Mg from the MgO shell can account for the variation in the reaction kinetics observed upon cycling, the complex

structure of the powder particles is still playing a role in defining the reaction kinetics. The behavior of these samples after a higher number of cycles is under investigation.

The behavior of doped Mg is different from what displayed by pure Mg even after cycling, so that we can infer that the catalyst particles, even if trapped inside the MgO shell, are still playing a role speeding the reaction kinetics with respect to pure Mg. On the other hand, the evolution of the microstructure has to be taken into account when defining the way of distributing the catalyst particles in the Mg material, and probably most of the studies on the efficiency of different kind of catalyst have to be reconsidered in the light of possible structural evolution during the life of technological devices.

3. Experimental Section

3.1. Synthesis of Nanocomposites

The experimental work was carried out on pure MgH_2 powders (Th. Goldschmidt, containing 5 wt% Mg as impurity) and on MgH_2 doped with 5 wt% of Fe (Noah Chemical, 200 mesh, 99.95 wt%). Both materials were processed by ball milling in a steel vial for 10 h in a Spex 8000 mixer-mill under 6 bar of pure Argon with a ball to powder ratio of 10:1.

3.2. H_2 Cycling

The cycles of hydrogen adsorption and desorption were performed in a Sievert's volumetric apparatus (Hydrogen Sorption Analyzer by Cantil srl). The same apparatus was used to monitor the reaction kinetics and the hydrogen storage capacity.

Fe-doped MgH_2 powder was heated at the temperature of 300 °C under 3.0 bar of H_2 in absorption reaction and 0.2 bar in desorption reaction. Every cycle was stopped after full absorption of the material; the cycle procedure was performed for 1, 22 and 47 cycles for the successive microscopic examination.

For pure MgH_2 , the temperature cycling was 350 °C because of its lower reactivity. In order to keep roughly constant the thermodynamic driving force, estimated according to the formulation of Rudman *et al.* [27] the cycling was induced by switching the pressure between 10 bar and 0.1 bar for 22 cycles.

3.3. Kinetic Analysis

Kinetics data was evaluated by curve-fitting procedure using the Johnson-Mehl-Avrami (JMA) theory [15–17]. The model describes a process of nucleation and growth where the transformed fraction $f(\alpha)$ is given by $f(\alpha) = 1 - \exp[-(kt)^n]$, where k is the rate constant and n , the so called the Avrami exponent, gives information about the rate limiting step of the reaction. In fact, the Avrami exponent n is given by $n = a + bc$ where a is related to the nucleation mechanism ($a = 0$ for instant nucleation, $0 < a < 1$ for decreasing nucleation rate; $a = 1$ for constant nucleation rate; $a > 1$ for increasing nucleation rate), c to the dimensionality of the growth process while b depends on the process controlling the flux of the reacting elements. In particular $c = 1$ describes a material flux controlled at an interface while $c = 0.5$ indicates a diffusion flux controlled by the Fick's law. The value of n , coupled, when available, with the apparent activation energy of the reaction is used to identify the rate limiting step which represents the slowest process in the sequence of reactions leading

to the phase transformation. The choice of the fitting model has been performed on the basis of the ability in reproducing actual experimental data. In fact, the other models taken into account, such as the contracting volume and surface reaction model [10,28], showed much worse fit indexes.

3.4. SEM Observation

Microscopic observations were carried out in order to characterize both the evolution of the sample morphology and the modifications of the internal microstructure. In the former case a small amount of powder has been directly deposited on a microscope stub, while in the latter, in order to expose the internal microstructure, on a polished sample, the powder was embedded in an Al matrix by the already described method [29]. SEM observations have been performed with a ZEISS EVO MA15, equipped with EDS analysis, operating at 20 kV.

4. Conclusions

In the present paper we have studied the effect of repeated hydrogen adsorption and desorption cycles on the structure and the hydrogen storage performances of Mg powders catalyzed by a homogeneous dispersion of Fe particles.

The kinetics of reaction with hydrogen appear to be accelerated by the repeated cycling, while the maximum storage capacity appears to be largely unaffected. The evolution of the characteristic parameters describing the reaction kinetics indicate that the rate limiting step of the reaction is affected both during hydrogen absorption and desorption, probably owing to the morphological and structural evolution of the powder material, while the maximum storage capacity is largely unaffected.

Besides a particle coarsening, a major effect on particle morphology is the progressive extraction of Mg from the MgO shell surrounding the powder particles. On one hand the catalyst particles are observed to concentrate at the hydride particle interior while on the other, fresh Mg not coated by the MgO crust can directly react with hydrogen. The extraction of Mg from the MgO crust, driven by the hydrogenation reaction, can therefore represent a possible strategy for an “*in situ*” purification of Mg based powder which is generally coated by an oxide layer, owing to the high reactivity with oxygen and moisture. The entity of this effect is probably related to the details of the diffusion mechanisms of Mg and H into the nano-crystal MgO crust even if a full explanation of this point would require a further investigation. The storage capacity and the H₂ sorption kinetics are not strongly affected by cycling probably also due to the higher reactivity of fresh Mg formed during cycling.

The Mg extraction from the MgO shell leaves the catalyst particles inside the hydride particles. This effect implies that the strategies for catalyst dispersion into the base material, in order to impart optimum performances, have to take into account this kind of possible in-service modification of the powder structure.

In conclusion we have demonstrated that the study of the morphological and structural modification of Mg based material upon cycling with hydrogen has to be considered as a necessary step toward the realization of technologically useful devices.

Acknowledgments

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Conflict of Interest

The authors declare no conflict of interest.

References

1. Zuttel, A. Hydrogen-storage materials for mobile applications. *Nature* **2001**, *414*, 353–358.
2. Goodell, P.D. Stability of rechargeable hydriding alloys during extended cycling. *J. Less Common Met.* **1984**, *99*, 1–14.
3. Dehouche, Z.; Djaozandry, R.; Huot, J.; Boily, S.; Goyette, J.; Bose, T.K.; Schulz, R. Influence of cycling on the thermodynamic and structure properties of nanocrystalline magnesium based hydride. *J. Alloys Comp.* **2000**, *305*, 264–271.
4. Bogdanovic, B.; Hartwig, T.H.; Spliethoff, B. The development, testing and optimization of energy storage materials based on the MgH_2/Mg system. *Int. J. Hydrogen Energy* **1993**, *18*, 575.
5. US Department of Energy website. Available online: <http://www.energy.gov> (accessed on 19 September 2012).
6. Huot, J.; Liang, G.; Boily, S.; van Neste, A.; Schulz, R. Structural study and hydrogen sorption kinetics of ball-milled magnesium hydride. *J. Alloys Comp.* **1999**, *293–295*, 495–500.
7. Jung, K.S.; Lee, E.Y.; Lee, K.S. Catalytic effects of metal oxide on hydrogen absorption of magnesium metal hydride. *J. Alloys Comp.* **2006**, *421*, 179–184.
8. Zaluska, A.; Zaluski, L.; Ström-Olsen, J.O. Nanocrystalline magnesium for hydrogen storage. *J. Alloys Comp.* **1999**, *288*, 217–225.
9. Kanoya, L.; Hosoe, M.; Suzuki, T. Development of High-capacity MgMH alloy for hydrogen. Storage. *Honda R D Tech. Rev.* **2002**, *14*, 91–98.
10. Oelerich, W.; Klassen, T.; Bormann, R. Metal oxides as catalysts for improved hydrogen sorption in nanocrystalline Mg-based materials. *J. Alloys Comp.* **2001**, *315*, 237–242.
11. Liang, G.; Huot, J.; Boily, S.; van Neste, A.; Schulz, R. Catalytic effect of transition metals on hydrogen sorption in nanocrystalline ball milled MgH_2 -Tm (Tm = Ti, V, Mn, Fe and Ni) systems. *J. Alloys Comp.* **1999**, *292*, 247–252.
12. Dehouche, Z.; Peretti, H.A.; Hamoudi, S.; Yoo, Y.; Belkacemi, K. Effect of activated alloys on hydrogen discharge kinetics of MgH_2 nanocrystals. *J. Alloys Comp.* **2008**, *455*, 432–439.
13. Bobet, J.-L.; Akiba, E.; Nakamura, Y.; Darriet, B. Study of Mg-M (M = Co, Ni and Fe) mixture elaborated by reactive mechanical alloying—Hydrogen sorption properties. *Int. J. Hydrogen Energy* **2000**, *25*, 987–996.
14. Vittori Antisari, M.; Aurora, A.; Mirabile Gattia, D.; Montone, A. On the nucleation step in the Mg– MgH_2 phase transformation. *Scripta Mater.* **2009**, *61*, 1064–1067.
15. Avrami, J. Kinetics of phase change. I: General theory. *J. Chem. Phys.* **1939**, *7*, 1103–1112.
16. Avrami, J. Kinetics of phase change. II Transformation-time relations for random distribution of nuclei. *J. Chem. Phys.* **1940**, *8*, 212–224.

17. Avrami, J. Granulation, phase change, and microstructure kinetics of phase change. III. *J. Chem. Phys.* **1941**, *9*, 177–184.
18. Vittori Antisari, M.; Montone, A.; Aurora, A.; Mancini, M.R.; Mirabile Gattia, D.; Pilloni, L. Scanning electron microscopy of partially de-hydrogenated MgH_2 powders. *Intermetallics* **2009**, *17*, 596–602.
19. Tien, H.Y.; Tanniru, M.; Wu, C.Y.; Ebrahimi, F. Mechanism of hydrogen capacity dependence on the hydrogenation temperature. *Scripta Mater.* **2010**, *62*, 274–277.
20. Polanski, M.; Bystrzycki, J.; Varin, R.A.; Plocinski, T.; Pisarek, M. The effect of chromium (III) oxide (Cr_2O_3) nanopowder on the microstructure and cyclic hydrogen storage behavior of magnesium hydride (MgH_2). *J. Alloys Comp.* **2011**, *509*, 2386–2391.
21. Agarwal, S.; Aurora, A.; Jain, A.; Jain, I.P.; Montone, A. Catalytic effect of ZrCrNi alloy on hydriding properties of MgH_2 . *Int. J. Hydrogen Energy* **2009**, *34*, 9157–9162.
22. Montone, A.; Aurora, A.; Mirabile Gattia, D.; Vittori Antisari, M. On the barriers limiting the reaction kinetics between catalysed Mg and hydrogen. *Scripta Mater.* **2010**, *63*, 456–459.
23. Liang, G.; Huot, J.; Boily, S.; van Neste, A.; Schulz, R. Hydrogen storage in mechanically milled Mg-LaNi_5 and $\text{MgH}_2\text{-LaNi}_5$ composite. *J. Alloys Comp.* **2000**, *297*, 261–265.
24. Malka, I.E.; Bystrzycki, J.; Płociński, T.; Czujko, T. Microstructure and hydrogen storage capacity of magnesium hydride with zirconium and niobium fluoride additives after cyclic loading. *J. Alloys Comp.* **2011**, *509*, S616–S620.
25. Jain, I.P.; Lal, C.; Jain, A. Hydrogen storage in Mg: A most promising material. *Int. J. Hydrogen Energy* **2010**, *35*, 5133–5144.
26. Pasquini, L.; Montone, A.; Callini, E.; Antisari, M.V.; Bonetti, E. Formation of hollow structures through diffusive phase transition across a membrane. *Appl. Phys. Lett.* **2011**, *99*, doi: 10.1063/1.3610973.
27. Rudman, P.S. Hydrogen-diffusion-rate-limited hydriding and dehydriding kinetics. *J. Appl. Phys.* **1979**, *50*, 7195–7199.
28. Mintz, M.; Zeiri, Y. Hydriding kinetics of powders. *J. Alloys Comp.* **1995**, *216*, 159–175.
29. Montone, A.; Vittori Antisari, M. A new method for preparing powders for transmission electron microscopy examination. *Micron* **2003**, *34*, 79–83.