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Catalytic effect of Pd on hydrogen absorption in mechanically alloyed Mg_2Ni, $LaNi_5$ and FeTi

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Abstract

In this paper we present the effect of palladium catalysis on the surface activity of nanocrystalline materials. Three classic hydrogen-absorbing alloys, Mg_2Ni, $LaNi_5$ and FeTi, were prepared in a nanocrystalline state by ball milling and modified by the addition of small amounts of Pd (less than 1 wt.%). This modification gave powders able to absorb hydrogen at room temperature in the as-produced state, with no need for any activation. Hydrogen absorption characteristics for the nanocrystalline Mg_2Ni, $LaNi_5$ and FeTi were enhanced: the absorption rates were much faster, even at lower temperatures.

Keywords: Palladium catalysis; Hydrogen absorption; Mechanical alloying; Ball milling

1. Introduction

Intermetallic compounds for hydrogen storage applications, e.g. Mg_2Ni, $LaNi_5$ and FeTi, have been investigated for about two decades [1–3]. One of the most serious problems with these materials is that they do not absorb hydrogen under normal conditions and have to be activated prior to hydrogenation. The activation process is usually complicated, involving repeated annealing at high temperature and/or pressure.

Recently nanocrystalline powders (with grain size less than 100 nm) have been developed for hydrogen storage. These materials are typically fabricated by using high-energy ball-milling [4–6]. This technique produces nanocrystalline material through cyclic mechanical deformation, starting either with a pre-prepared alloy or with a mixture of pure elemental metals. For materials which are difficult to obtain by classic metallurgical methods (as for example Mg_2Ni), being able to start from the elemental powders is advantageous.

Nanocrystalline alloys investigated so far (FeTi [4,5], Mg_2Ni [6]) showed much easier activation than their conventional polycrystalline counterparts. For example, the activation procedure for polycrystalline FeTi requires heating up to 400–450 °C in vacuum and subsequent annealing in H_2 at pressure of about 7 bar, followed by cooling down to room temperature and exposure to hydrogen at high pressure (35–65 bar) [2]. The activation process has to be repeated several times to obtain reproducible pressure–concentration isotherms. However, in the case of ball-milled nanocrystalline FeTi a single annealing at 400 °C for 0.5 h in vacuum is sufficient to obtain full hydrogen absorption cycles [4,5]. Similar results for ball-milled Mg_2Ni are also found [6].

A critical factor for hydrogen absorption by metals is the metal surface, which should be able to dissociate the hydrogen molecules and also allow easy penetration of hydrogen into the bulk. In practice it is very difficult to avoid surface contamination of the sample during synthesis of the material and handling. The obvious solution is to maintain ultra high vacuum conditions, but this is very expensive and may be limited to laboratory-scale samples. Even short exposure to air poisons the material and in many cases prevents absorption of hydrogen by the material. To restore good hydrogen sorption properties some kind of activation procedure has to be applied. Ball milling constantly creates fresh surfaces during the processing, as a result of repeated cold welding and fracture. This and the high surface-to-volume ratio explains why the activation procedure may be much easier in the case of the ball-milled powder than that for classic polycrystalline material.

Another way to enhance hydrogen absorption and overcome the problem of surface poisoning is catalysis. Catalytic effects of metals on hydrogen dissociation have

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been presented in [7]. It was shown for the heavily contaminated metal film samples that the presence of Pd, Ni or Fe overlayer (about 3 nm thick) enhances hydrogen absorption. These results indicated that the poisoning of the sample surface is caused by the reduced dissociation of the hydrogen molecules on the oxidized metal surfaces. Palladium is an especially good catalyst for hydrogen dissociation reaction. The reactivity of palladium after exposure to oxygen is recovered during exposure to hydrogen because of the easy decomposition of the palladium oxide. Cycling test experiments performed with mixtures of hydrogen absorbers and palladium catalyst also demonstrated that Pd improved hydrogenation [7].

In this paper we report on the effects of palladium on the surface activity of nanocrystalline materials. We show that activation may be totally avoided by adding small amounts of palladium to the metal powders. This simple method gives material able to absorb hydrogen at room temperature with no need for any activation. We also observed hydrogen absorption at room temperature in nanocrystalline materials with no added Pd, after short exposure to air, although the reaction rate was much slower than for samples modified with palladium.

2. Experimental methods

Nanocrystalline Mg_2Ni, FeTi and amorphous FeTi powders were fabricated from elemental powders of high purity by high-energy ball milling [4–6]. $LaNi_5$ powder was produced from the alloy premelted in an arc furnace. The milling was carried out using a high-energy ball mill from Spex (Spex 8000). Powder mixtures were sealed in the tungsten carbide or hardened steel vials under argon atmosphere. The handling of the samples was done in an argon-filled glove box. Modification of the surface of the material was done by means of introducing small amounts of Pd (less than 1 wt.%) to the powders in the course of the ball-milling process. The method is similar to that proposed by Harris et al. [8] for producing compositionally graded amorphous materials. Ball-milled powders were characterized by X-ray diffraction technique using a Nicolet-Stoe powder diffractometer (Cu Kα radiation). The microstructures and phase compositions of the ball-milled material were studied using a Philips CM20 (200 kV) transmission electron microscope equipped with an energy-dispersive X-ray analysis system (EDAX 9900) with a thin Be window. Grain size of the powders was determined both from TEM and from the X-ray diffraction (by measuring broadening of the diffraction peaks after subtraction a contribution from strain). Hydrogen sorption properties of the ball-milled powders and of the alloys prepared by arc melting were investigated by an automated computer-controlled gas titration apparatus, similar to that described in [9].

3. Results and discussion

3.1. Nanocrystalline Mg_2Ni

High hydrogen capacity (4 atoms of hydrogen per Mg_2Ni) combined with the small specific weight of the alloy is the most important advantage of Mg_2Ni. Nanocrystalline Mg_2Ni (with grain size of about 20–30 nm) exhibits significantly improved activity and hydrogen absorption kinetics, as compared to the polycrystalline material, as we showed in [6]. Modification of this material by palladium gives further improvement of the hydrogenation characteristics. All the results presented here for the Pd-modified Mg_2Ni were obtained without any prior activation of the material (i.e. annealing or any exposure to hydrogen). After preparation the powder was kept in air, without any protection. It was then placed in the hydrogenation system and the absorption characteristics were measured.

It is well established that the classic polycrystalline Mg_2Ni absorbs hydrogen (under moderate pressure of hydrogen: less than 20 bar) only at high temperatures. The temperature required for hydrogenation is typically 300 °C. This temperature is probably related to the transformation temperature of the Mg_2NiH_4 hydride, 225 °C. Above this temperature a cubic Mg_2NiH_4 forms with $a = 0.6490$ nm [10]. Below 225 °C a low-temperature hydride is stable, with a more complicated, twinned structure [11, 12]. Formation of the high-temperature form of Mg_2NiH_4 is apparently much easier than the low-temperature modification, and the latter is practically unattainable by hydrogenation under moderate pressure conditions. Our results show that nanocrystalline Mg_2Ni modified by Pd can be reversibly hydrogenated (without activation) at temperatures lower than 225 °C, i.e. below the transformation temperature of the hydride. Fig. 1(b) presents an absorption curve obtained at 200 °C. The absorption kinetics are very fast (2 hydrogen atoms per formula unit in 2 min) and are reproducible after desorption at the same temperature under vacuum. However, the hydrogen content after apparent saturation (hydrogenation time 30 min) is less than the hydrogen content in nanocrystalline Mg_2Ni hydrogenated at high temperature (Fig. 1(a)). The reason for this lower hydrogen capacity is still under investigation and may be related to slower diffusion of hydrogen through the initially formed layer of Mg_2NiH_x. As can be seen from the literature, even at 300 °C the full nominal amount of hydrogen in Mg_2Ni (i.e. 4 atoms per Mg_2Ni) is difficult to obtain in practice. Usually the total hydrogen content equals about 3.0–3.45 wt.% in the reported reversible hydro-

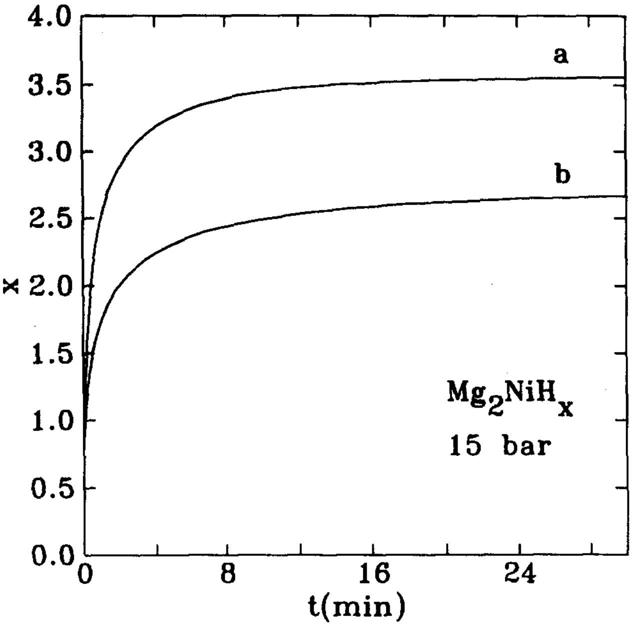


Fig. 1. Rate of hydrogen absorption by (a) nanocrystalline Mg_2Ni at 300 °C and (b) nanocrystalline Mg_2Ni with Pd at 200 °C.

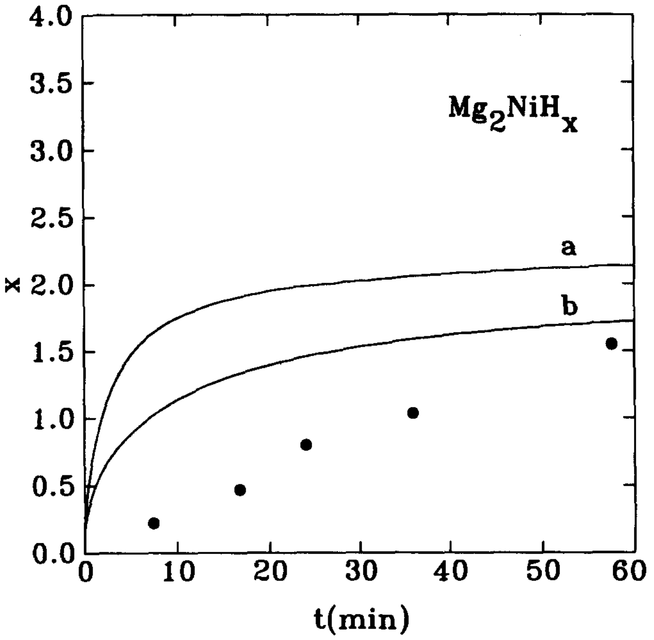


Fig. 2. Rate of hydrogen absorption by nanocrystalline Mg_2Ni modified with Pd in the as-ball-milled state (room temperature, 12 bar). Curves (a) and (b) represent two different modification process. Dots show results for HCl-etched polycrystalline Mg_2Ni [15].

genation cycles [13,14], compared with the nominal value of 3.6 wt.%.

Nanocrystalline Mg_2Ni modified by Pd absorbs hydrogen even at room temperature without any activation. Room-temperature absorption is relatively fast, and absorption of up to 2 hydrogen atoms per Mg_2Ni formula unit can be reached in 27 min (Fig. 2(a)). Hydrogen absorption kinetics, as well as reproducible hydrogen capacity, are very sensitive to the way nanocrystalline Mg_2Ni material is prepared with the Pd additive. Curves (a) and (b) in Fig. 2 show a comparison of the best sample so far with a sample prepared with only slightly lower Pd content (curve b). Fig. 2 also presents results in the literature [15] for the room-temperature absorption of Mg_2Ni obtained for the polycrystalline powder etched in HCl before absorption under hydrogen pressure of 40 bar. Absorption kinetics are slow in this case, although after a long time (5 h) a capacity of 3.0 hydrogen atoms per Mg_2Ni is reached (not shown in the figure). Subsequent cycles, however, exhibited a gradual deterioration of hydrogen absorption [15]. The authors suggest that selective etching formed nickel particles on the surface, thus catalyzing dissociation of hydrogen. Cycling causes the powder particles to break off and the formation of new, less active, surfaces. Room-temperature absorption of hydrogen was also recently reported on Mg_2Ni and FeTi [16] ball milled in argon and hydrogen atmosphere or in vacuum (with no exposure to air). The authors suggest that easier hydrogen absorption in these materials is related to fresh surfaces and cracks, created in the ball-milling process.

3.2. Nanocrystalline $LaNi_5$

$LaNi_5$ is a good example of a metal which is known to absorb hydrogen at low temperature. For $LaNi_5$ the activation process prior to hydrogenation (although much easier than for Mg_2Ni and FeTi) is still necessary. The activation procedure consists of a long exposure to hydrogen at high pressure (50 bar) at room temperature [3]. Wang and Suda [17] found very good activity to hydrogen uptake in chemically treated $LaNi_{4.7}Al_{0.3}$ alloy. They suggest that the good catalytic properties of chemically treated surfaces are related to the Ni-rich sublayer formed during the treatment. Our results show that the combination of ball milling and catalytic effect of Pd can give significant enhancement of the activity and absorption kinetics of $LaNi_5$. Fig. 3 shows the results for three $LaNi_5$ samples. Curve (a) represents the sample prepared by ball milling, but then stored in air for several months. Hydrogen absorption began after a long incubation time and was saturated after 17 h, which is comparable with the classic polycrystalline material. Curve (b) was obtained for the freshly ball-milled material, exposed to air for only a short time during handling. The incubation period is short, about 7 min, but the absorption kinetics are still relatively slow (half reaction time $t_{1/2}=25$ min). Curve (c) in Fig. 3 shows an excellent hydrogenation behavior of the $LaNi_5$ sample ball-milled and modified with Pd. There is no incubation time in this case and hydrogen absorption is very fast, with $t_{1/2}=22$ s.

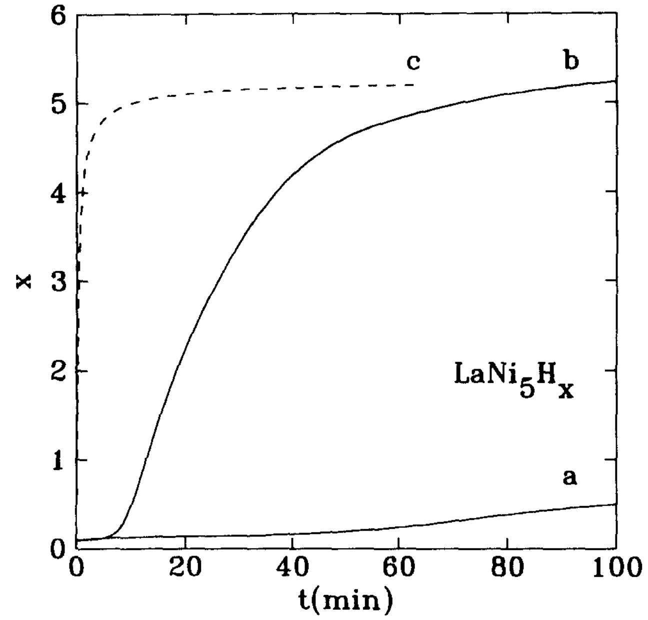
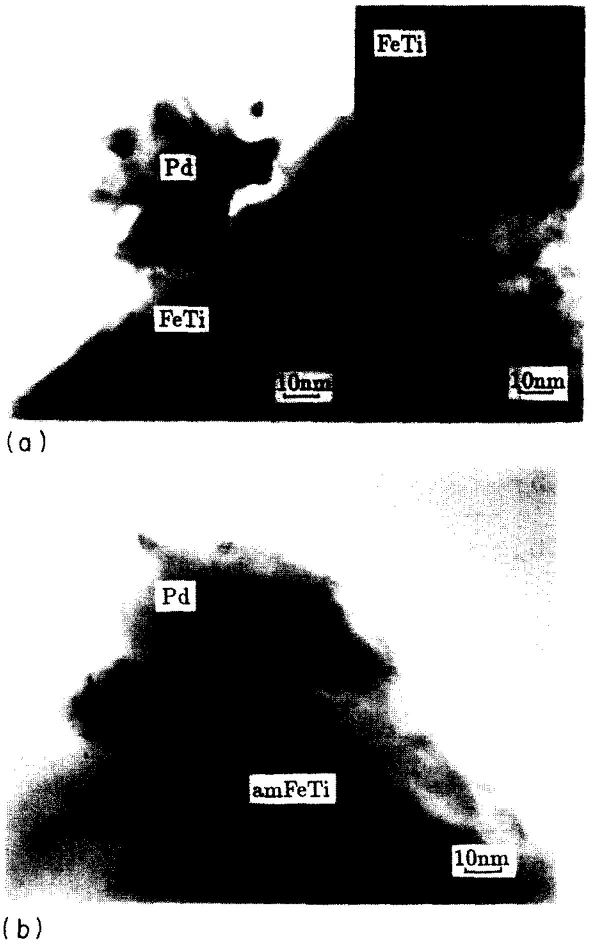


Fig. 3. Rate of hydrogen absorption by $LaNi_5$ measured at 40 °C: (a) sample stored in air for several months; (b) freshly ball-milled; (c) modified with Pd (hydrogenation pressure 15 bar).

3.3. Nanaocrystalline and amorphous FeTi

Hydrogenation characteristics of nanocrystalline FeTi with grain sizes of about 6–7 nm (after activation involving a single annealing at 400 °C for 0.5 h) have been previously presented in [4,5]. This behavior showed a relatively large solubility region (up to 0.3H/FeTi) and plateau pressure at 7 bar, lower than the absorption pressure of the conventional alloy. Modification of this alloy by a small amount of Pd drastically changes the hydrogen sorption properties. Palladium-modified nanocrystalline FeTi readily absorbs hydrogen at room temperature with neither thermal activation (annealing under vacuum) nor previous exposure to high pressure of hydrogen. The hydrogen uptake equals about 0.5 hydrogen atom/FeTi at pressures lower than 1 bar and 0.9H/FeTi at hydrogenation pressure of 10 bar. There is no well-defined plateau in the pressure–concentration isotherm (in the as-received state). As we discuss in forthcoming paper [18] this absorption behavior may be attributed to the structural state of the as-ball-milled material, which may be relaxed by the activation annealing.

Amorphous ball-milled FeTi powder does not absorb hydrogen unless annealed at 300 °C for 0.5 h [4,5]. After activation, amorphous FeTi exhibits hydrogenation characteristics typical for amorphous materials: a monotonic increase of hydrogen content with the logarithm of applied pressure [4,9,19] with no plateau. The palladium-modified material absorbs hydrogen without any activation, and the pressure–concentration isotherm is shifted towards higher hydrogen concentration (by about 0.15H/FeTi). This enhanced hydrogen absorption for the as-ball-milled amorphous material may be caused by lower density of the unrelaxed material [18].



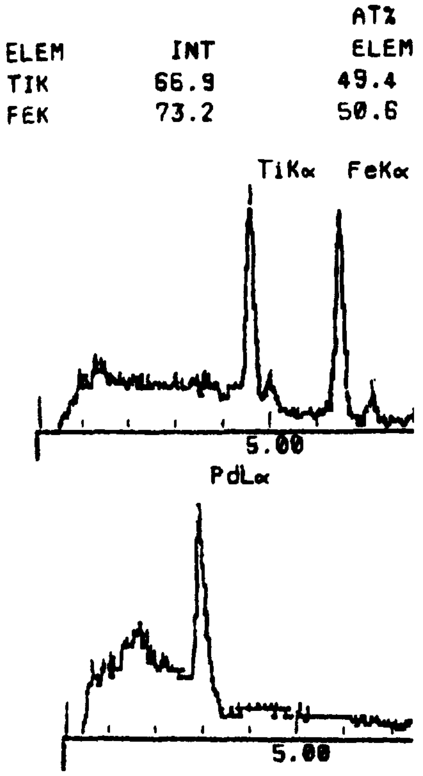
(a)

(b)

Fig. 4. TEM images of (a) the nanocrystalline and (b) amorphous FeTi samples with clusters of palladium.

3.4. Mechanism of Pd catalysis

Pd catalysis is clearly very effective in enhancing the kinetics of hydrogen absorption of metallic hydrogen storage materials. In all cases there is no need for activation prior to hydrogenation. As a consequence, hydrogen absorption could be improved (which means absorption of higher hydrogen concentration and at lower pressures and lower temperatures). Absorption kinetics were enhanced in some cases, however, at the expense of reduced hydrogen capacity. To examine the role of palladium further, microstructure studies of the Pd-modified powders were performed. X-ray diffraction did not reveal any clear peak due to Pd because of the very small palladium content in the powder (less than 1 wt.%). As shown by TEM, microstructures of the powders are very similar to the nanocrystalline materials without Pd modification. In the case of FeTi the average grain size was equal to 6–7 nm and about



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                        AT%
ELEM        INT         ELEM
TIK         66.9        49.4
FEK         73.2        50.6
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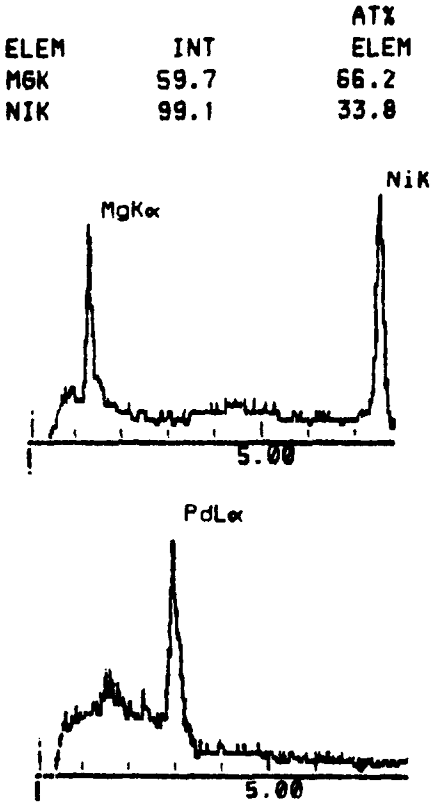
Fig. 5. EDX spectra for the Pd cluster and FeTi.

Fig. 6. TEM image of nanocrystalline Mg_2Ni with Pd, and electron diffraction pattern of Mg_2Ni.



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                        AT%
ELEM        INT         ELEM
MGK         59.7        66.2
NIK         99.1        33.8
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Fig. 7. EDX spectra for the Pd particle and Mg_2Ni.

20–30 nm for Mg_2Ni. $LaNi_5$ exhibited a greater distribution in grain size: between 30 and 80 nm. The less uniform microstructure of the $LaNi_5$ was a result of the relatively short milling time applied in this case. For all the alloys TEM studies revealed a similar mechanism for Pd catalysis. Introduction of palladium into the powder in the course of ball-milling does not coat the powder with a uniform Pd layer. Instead, small clusters of Pd are attached (cold welded) to the powder particles. Each palladium cluster (of the average size of about 100 nm) consists of 20–50 nm Pd crystallites. There is no indication of an alloying zone between palladium and the main component of the powder. Fig. 4 shows the palladium particles attached to the nanocrystalline and amorphous FeTi powders. Fig. 5 shows EDX spectra for the Pd cluster and for FeTi. Similar microstructures have been observed for Mg_2Ni (Figs. 6 and 7) and $LaNi_5$ powders. TEM results suggest that the mechanism of the catalysis may be caused by a "spillover" effect [7,20]. Palladium catalyzes the dissociation of H_2, and the adsorbed hydrogen atoms can be spilled over onto the surface of the material. The Pd catalyst may thus be effective when present in the form of small clusters or particles dispersed on the surface of the absorbing material, leaving no need for the formation of the Pd layer.

There are two important advantages of this catalysis mechanism. The first is that the negative effect of poisoning of the metal surfaces may be eliminated for all practical purposes. Preparation of the material and handling can be done without too much care about oxygen-free conditions. Effects of the metal surface contamination are eliminated by the catalytic action of palladium. We checked the efficiency of this process even on samples as old as about two years, stored in air without any protection against the oxygen contamination and humidity. The second advantage of the "spillover" mechanism is that the effective amount of the catalyst can be very small: less than 1 wt.%, which does not significantly raise the total cost of the material.

4. Conclusions

The effects of palladium on the surface activity and absorption of hydrogen were shown for the three classic hydrogen absorbers: Mg_2Ni, $LaNi_5$ and FeTi, produced by ball-milling. The powders modified with Pd readily absorb hydrogen at room temperature with no activation applied. The materials show also substantially enhanced hydrogen absorption kinetics and are much less sensitive to air exposures, which normally poison the surface and create a barrier for hydrogen dissociation and transfer into the material. The effect of palladium catalysis was found to exhibit the spillover mechanism. The Pd catalyst acted effectively when present in the form of small clusters or particles dispersed on the surface of the absorbing material.

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