HYDROGEN STORAGE IN MAGNESIUM BASED ALLOYS

J. Grbović Novaković, Tanja Brdarić*, N. Novaković**, S. Mentus***

* VIN^A Institute of Nuclear Science, Laboratory for Material Sciences,
P.O. Box 522, Belgrade, Serbia, jasnag@vin.bg.ac.yu, tanjab@vin.bg.ac.yu
** VIN^A Institute of Nuclear Science, Laboratory for Nuclear and Plasma
Physic, P. O. Box 522, Belgrade, Serbia,novnik@vin.bg.ac.yu
*** Faculty of Physical Chemistry Belgrade, Belgrade
Serbia,slavko@ffh.bg.ac.yu

ABSTRACT

Hydrogen is a non-polluting fuel, but being a light gas it is too voluminous. Its flammability presents also a significant disadvantage. Consequently, effective and safe storage of hydrogen has challenged researchers world-wide for almost three decades. Metals can absorb hydrogen in atomic form and thereby act as hydrogen "sponges".Due to its high hydrogen storage capacity, light weight, low cost and abundance in the earth's crust, magnesium and magnesium based alloys are the most promising candidates for hydrogen storage materials. However, the hydriding/dehydriding reaction takes place at high temperature and the kinetic is relatively slow. One of the ways to improve the kinetics of magnesium based hydrogen storage materials is the addition of metals and/or metallic oxides. It has been revealed that ball milling of MgH_2 powders with small amounts of 3d-transition metals or their oxides leads to marked improvements of the hydrogen absorption/desorption kinetics.

It is worth to notice that the first-principles electronic simulations can offer great insight into the understanding of the influence of alloying elements on the hydride properties and guide the experimental research.

Key words: hydrogen storage, MgH_2, ball milling, catalyst, ab initio electronic structure calculation

Introduction

In the XX century the world economy is based completely, on use of oil and natural gas. Evident technical achievements of the XX century economy are

well known, but, at the same time, this economy permanently leads the humankind to the irreversible environmental catastrophe.

With the growing environmental concerns greenhouse gas emissions from the burning of fossil fuels, it is becoming increasingly important to switch to cleaner alternative fuels such as hydrogen. Even a small increase in the number of vehicles using hydrogen can lead to significantly reduces CO_2 and NOx emissions [1] A major bottleneck to ensure a smooth transitions to so-called hydrogen economy is a need for efficient on board hydrogen storage technologies [2-4]. The other important part of this transition is hydrogen production. The development of fuel cell powered vehicles has been an active area of research for the past 30 years and many automotive companies, such as, GM[5], BMW[6], Daimler Chrysler[7], Honda[8], Toyota [9], have come up with innovative design features in their prototypes. Most of the fuel cell cars utilize liquefied hydrogen or compressed hydrogen.

Pressurized hydrogen gas takes a great deal of volume compared with, for example, gasoline with equal energy content, about 30 times bigger volume at 100 bars gas pressure. Condensed hydrogen is about 10 times denser, but is much too expensive to produce and maintain [10]. The cost and energy consumption involved in producing compressed or liquefied hydrogen disable the wide utility of hydrogen as an efficient alternative fuel.

Table. 1 Physical and chemical properties of hydrogen and petrol		
Properties	Hydrogen (H_2)	Petrol ($-CH_2-$)
Lower heating value (kWh kg^{-1})	33.33	12.4
Self-ignition temperature (°C)	585	228-501
Flame temperature (°C)	2.045	2.200
Ignition limits in air (Vol%)	4-75	1.0-7.6
Minimal ignition energy (mW s)	0.02	0.24
Flame propagation in air (m s^{-1})	2.65	0.4
Diffusion coefficient in air (cm^2 s^{-1})	0.61	0.05
Toxicity	no	high

Hydrogen is a molecular gas. At room temperature and atmospheric pressure, 4 kg of hydrogen occupies a volume of 45 m^3. This corresponds to a balloon of 5 m diameter — hardly a practical solution for a vehicle (Table 1). There are also obvious safety concerns with the use of pressurized or liquefied hydrogen in vehicles. Therefore, developing effective hydrogen storage for transportation is a central challenge for basic research and a key factor in enabling the success of the hydrogen economy. The operating requirements for effective hydrogen storage for transportation include the following:

- Appropriate thermodynamics (favorable enthalpies of hydrogen absorption and desorption),
- Fast kinetics (quick uptake and release),
- High storage capacity (specific capacity to be determined by usage),
- Effective heat transfer,
- High gravimetric and volumetric densities (light in weight and conservative in space),
- Long cycle lifetime for hydrogen absorption/desorption,

Solid-state storage refers to the storage of hydrogen in metal hydrides, in chemical storage materials, and in nanostructured materials. This method of hydrogen storage offers perhaps the best opportunities for meeting the requirements for onboard storage. Reversible storage means that hydrogen is released by raising the temperature of, for example, a metal hydride at a suitable pressure; hydrogen is subsequently replaced (stored) through the control of temperature and hydrogen pressure. Ideally, storage and release of hydrogen should take place at temperatures between 0 °C and 100 °C and pressures of 1–10 bar and on time scales suitable for transportation applications. Some materials contain strongly chemically bound hydrogen that is not readily retrievable. Only hydrogen that can be made easily accessible will meet the hydrogen storage requirements.

Although, the hydrogen storage in carbon nanotubes, fullerens and other materials has been reported, this review will address metal hydrides only.

Formation of metal hydrides

Many metals and alloys are capable of reversibly absorbing large amounts of hydrogen according to the reaction (1):

$$Me + \frac{x}{2}H_2 \Leftrightarrow MeH_x \tag{1}$$

Here Me is a metal, a solid solution, or an intermetallic compound, MeH_x is the hydride and x the ratio of hydrogen to metal H/Me. In most, cases the reaction is exothermic and reversible. If we applied heat hydrogen is desorbed again.

Charging can be done using molecular hydrogen gas or hydrogen atoms from an electrolyte. If hydrogen is loaded from gas phase several reaction stages of hydrogen with metal occurred as it showed in Fig.1.
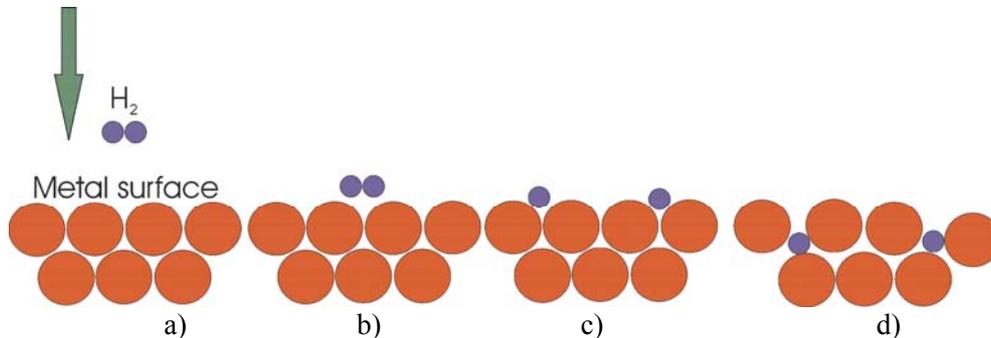
Fig 1. Reaction of H₂ molecule with a storage material. a) H₂ molecule approaching the metal surface. b) interaction of H₂ molecule by Van der Waals forces (physisorbed state) c) chemisorbed hydrogen after dissociation d) occupation of subsurface sites and diffusion into bulk. In many cases hydrogen occupies interstitial sites – tetrahedral or octahedral-in the metal host lattice. While in the first the hydrogen atom is located inside a tetrahedron formed by four metal atoms, in the latter the hydrogen atom is surrounded with six metal atoms forming an octahedron

The first attractive interaction of hydrogen molecule approaching the metal surface is Van der Waals force, leading to a physisorbed state. The physisorption energy is typically of order $E_{phys} \approx 10 \, KJ/mol$. In the next step the hydrogen has to overcome an activation barrier for dissociation and for the formation of the hydrogen metal bond. This process is called chemisorption. The chemisorption energy is typically of order $E_{phys} \approx 50 \, KJ/mol$. After dissociation on the metal surface, the H atoms generally diffuse rapidly through the bulk metal even at room T to form M-H solid solution, etc. α- phase. The thermodynamic aspects of hydride formation from gaseous hydrogen are described by pressure –composition isotherms (Fig. 2). When the maximum solubility of hydrogen in the α–phase is reached, the hydride phase (β–phase) will start forming. Increasing the hydrogen pressure further will now result in a substantial increase in the absorbed amount of hydrogen.

This phenomenon may be explained from the Gibbs phase rule (2)

$$F = 2 - \pi + N \tag{2}$$

where F is the degree of freedom, π is the number of phases and N is the number of chemical species.

The pressure at which this transformation takes place is referred as the plateau pressure and in this region the α-phase and β-phase co-exist. When the stoichiometric hydrid have formed completely depleting the β-phase one additional degree of freedom is regained and the additional absorption of hydrogen will now

require a huge pressure increase. This corresponds to the solid solution of hydrogen in the β-phase. The plateau pressure, described by van't Hoff equation (3), gives us valuable information about reversible storage capacity from the width of the plateau and the position of the plateau at a given temperature may give an idea of the stability of the hydride. Stable hydrides (Hf << 0) will require higher temperatures than less stable hydrides (Hf < 0) to reach a certain plateau pressure. Making series of PCI's at different temperatures it is even possible to construct a phase diagram from the end points of the plateaus in the individual PCI's.
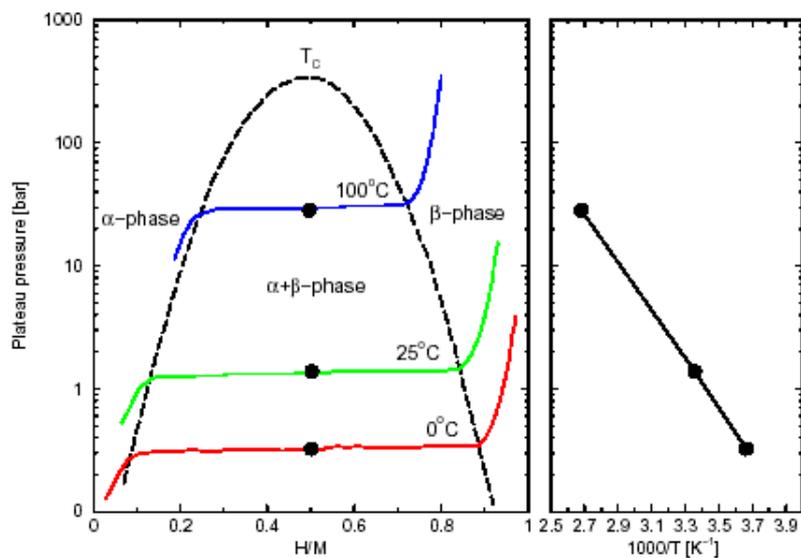

Fig. 2. Left: Pressure-Composition-Isotherms (PCI) for a hypothetical metal hydride. Adapted from ref. [1,2]. Right: Van't Hoff plot for a hypothetical metal hydride derived from the measured pressures at plateau midpoints from the PCI's

$$\ln p = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \tag{3}$$

Where ΔH is enthalpy, ΔS is entropy, R is gas constant and T is temperature.

Figure 3 is a van't Hoff diagram showing the dissociation pressures and temperatures of a number of hydrides. Light elements, such as Mg, have shown promising levels of stored hydrogen (about 7 wt% hydrogen), but they release hydrogen at high temperature.

Conventional metal hydrides, which are well characterized and have well-established values for interstitial hydrogen storage, include intermetallics of the types AB, AB_2, AB_5, A_2B, and body-centered cubic metals. These materials

typically store between 1.4 and 3.6 wt% hydrogen. Examples of these intermetallic compounds are TiFe, $ZrMn_2$, $LaNi_5$, and Mg_2Ni.

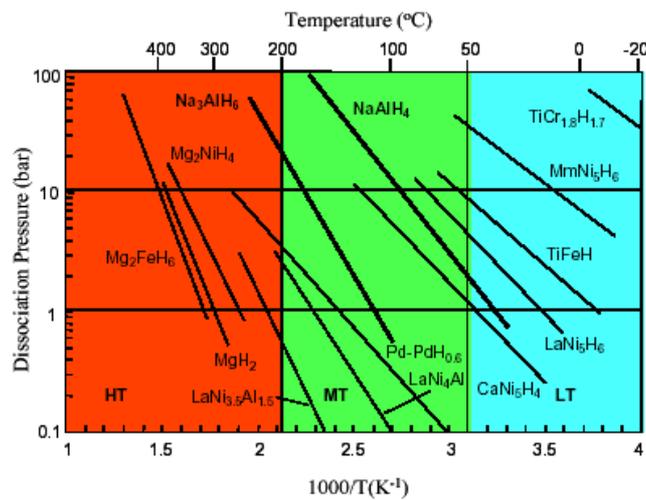| Table 2. Hydrogen storage properties of some intermetallic compounds				
Maximim hydrogen capacity				
Type	Intemetallic	H/M^a	Wt%	Temperature (K) for 1 atm $P_{dessorption}$
A_2B	Mg_2Ni	1.33	3.6	528
AB	TiFe	0.975	1.86	265
AB	ZrNi	1.4	1.85	565
AB_2	$ZrMn_2$	1.2	1.77	440
AB_5	$LaNi_5$	1.08	1.49	285
AB_2	$TiV_{0,62}Mn_{1,5}$	1.14	2.15	267

Fig.3. van't Hoff Diagram Showing Dissociation Pressures and Temperatures of Various Hydrides [1,2]

Their hydrogen storage properties are listed in Table 2.But one can see, that demand for gravimetric capacity, fast kinetic and high storage capacity is barely satisfied, so development of new light weight materials presents many scientific and technical challenges.

Among, metal hydrides, particularly magnesium hydride, appears to be the most attractive one because of its high storage capacity and low cost. Unfortunately, the poor hydruration characteristics of magnesium have limited its applications so far.

Magnesium as a hydrogen storage material

An important parameter of hydrogen storage systems, especially for mobile applications, is the speed of hydriding. The goal is to store a few kg of hydrogen in a few minutes (when hydrogen is loaded in the form of a hydride the absorption rate can be smaller). As it was mentioned before the hydriding process involves the following steps: gas transport to the surface of the particles, surface adsorption and dissociation, transition from surface to bulk, diffusion through the material and finally nucleation and growth [11,12].

Usually these processes are relatively fast for practical-size batches, so that thermal conductivity and gas permeability are the limiting factors in applications [13]. In the shell model, hydride formation starts at the surface of a magnesium metal particle. When more than three of these hydride grains nucleate at the surface, they will eventually merge and form a gas-tight, closed shell (due to the low hydrogen mobility) of magnesium hydride around the remaining metal core [14-19]. Vigeholm et al. found that the diffusion of hydrogen is not through the magnesium hydride phase, but rather along the hydride-metal interface [14, 20].

Experimentally it has been found that for particles larger than about 75 μm, the hydriding progress becomes very slow when about 30% of the sample has converted to MgH_2 and that at the end theparticle still contains an unreacted magnesium metal core [11, 12].

The isolating effect of a hydride layer near the interface has also been observed in the case of thin magnesium layers [21]. On dehydriding, the magnesium hydride starts to convert to magnesium metal at the surface while the size of the magnesium hydride phase decreases. The hydriding and dehydriding processes may therefore be intrinsically asymmetric [17]. The importance of the dissociation process has been stressed by Gerasimov *et al.* [22]. They also found that cracking of the magnesium oxide layer occurs during a heat treatment, which makes the magnesium metal surface accessible for hydrogen molecules [23]. Mintz et al. showed that the diffusion process may be relevant [24]. Liang et al. found that initially nucleation and growth and in a later stage the long range hydrogen diffusion is most important [25].

Ball milling and catalysts

Recently, high energy ball milling was applied to magnesium hydride which decreases the particle size and induces stresses and defects in the structure [25, 26]. The ball milling treatment increases the hydriding kinetics by approximately a factor of 10. As ball milling breaks down the particles, a higher surface area is present for hydrogen to enter the particles. Other effects may be that hydrogen diffusion is speeded by the introduction of defect zones or that defects form multiple nucleation centers for MgH_2. Huot and co-workers investigated ball milled magnesium in detail using X-ray diffraction [26]. They found that a ball

milling treatment of β–MgH$_2$ forms the high pressure γ–MgH$_2$–phase to a concentration of 18%. Cycling the hydrogen content removes this phase again. The average particle size for such ball milled samples was determined to be 12 nm. The background of the diffraction patterns obtained after ball milling is significantly increased, which means that a large part of the scattering is not found in the Bragg peaks any more, possibly due to very small crystallites, very high defect concentrations, strongly distorted structures or amorphous parts in the crystallites. The fact that diffraction relies on long-range ordering is clearly a drawback when one wants to study materials which are heavily deformed (for instance by ball milling) Bur even, at nanoscale MgH$_2$ doesn't show the desirable characteristics for hydrogen storage materials Fig 4.
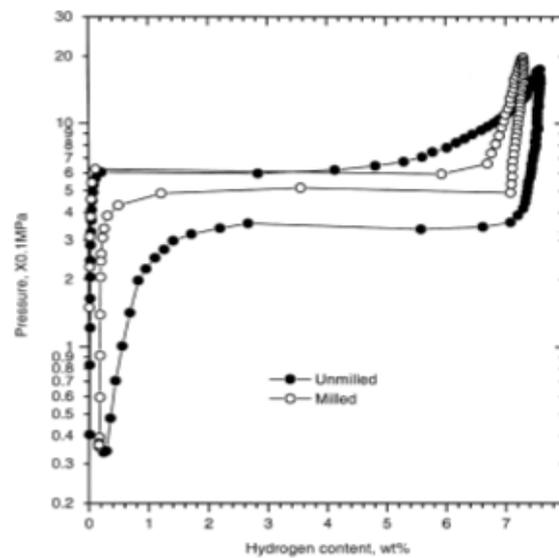

Fig.4. Pressure–concentration–temperature curves of the unmilled and ball-milled MgH$_2$ at 623 K. [26]

Substantial improvements in the hydriding-dehydriding kinetics has been accelerated significantly by adding to Mg based materials small amounts of catalyzing particles constituted either by: (i) metals (Ce, Ti, Nb, Fe, Co and Ni); (ii) nonmetals (C and Si); (iii) 3d transition metal oxides (TiO$_2$, V$_2$O$_5$, MnO$_2$, Fe$_2$O$_3$); (iv) intermetallic compounds (LaNi$_5$, Mg$_2$Ni, FeTi) [14, 27-30].

Among additives that can be used to improved hydrogen storage capacities metals can act through two different mechanisms: (a) metals like Ni, Pd or Ti form hydrides, which can behave as "hydrogen pumps"; (b) transition metals such as Fe, Co or Cr, which , favor the hydrogen molecule dissociation and the phase transformation of Mg matrix to MgH$_2$ [31].

In both cases the material performances depend, among other factors, on the optimization of the synthesis procedure and on amount of catalyst since both parameters play a critical role to obtain the best dispersion in matrix and optimum sorption properties.

An example of the effect of a hydride forming catalyst has been reported by Zaluski *et al.* [32] who studied the effect of small Pd addition to nanocrystaline hydrogen-absorbing alloys based on Mg_2Ni, $LaNi_5$. The experimental results show that even the addition of very small amounts of Pd (less than 1 wt%) allows hydrogen absorption at room temperatures without the need for any activation procedure.

As far as the transition metals are concerned, Bobet *et al.* [33] reported that the addition of Co or Fe during reactive ball milling of Mg significantly increases the quantity of formed MgH_2, since the processing was able to induce reduction of Mg particle size and easy formation of hydride phase. They were able to show that a proper microstructure with short hydrogen diffusion distances improves the hydrogen sorption kinetics.

Moreover, excellent performances were obtained also by adding more than one catalysing material like 1wt.% Ni - 0.2 wt.% Pd [34]. In this case, the combined effect of Pd and Ni induces fast nucleation sites for phase transformation during both absorption and desorption processes and even if nanocrystallinity of the powder is largely lost during heat treatments in H_2, the reaction kinetics remains excellent over more than 50 cycles.

In order to correlate the microstructure and the kinetics properties of this kind of composites, we have investigated the combined effect of the processing parameters and of the catalyst amount in MgH_2 doped with Co and Fe [35,36]. Accordingly, the amount of added metal catalyst (Fig. 5) and milling intensity (Fig. 6) have been changed in a systematic way in order to search for an optimized microstructure where the dispersion of the catalyst and the particle size can give rise to fast reaction with H_2. It has been found that inhomogeneous catalyst distribution results for a small amount (2 or 5 wt.%) of catalyzing metal and for a low value of the milling intensity (Ball to Powder Ratio-BPR- 1:1 or 3:1). In these cases large volumes free from catalyst are observed, which results in a two-step dehydrogenation process and only a fraction of the total hydrogen is released at temperatures lower than that characteristic for pure milled MgH_2.
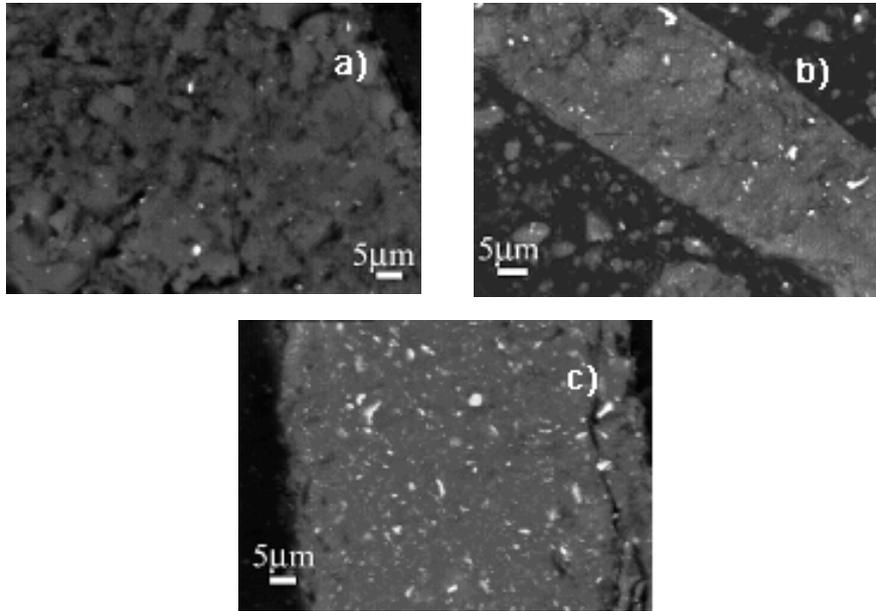
Fig. 5. SEM images of MgH$_2$ – Fe composite (BPR 10:1): a) 2 wt.% Fe, b) 5 wt.% Fe and c) 10 wt.% Fe [35].

A more homogeneous distribution of catalysing particles was achieved for samples containing at least 10 wt.% of metal catalyst (Co or Fe), milled under BPR of 10:1. In the case of Fe addition, process of dehydrogenation onsets at 493 K, probably at the Fe-MgH$_2$ interface. Optimum performances (Fig. 7) were obtained for the composite with 10 wt.% of Fe, where the particles are small (2-5 μm) and uniformly distributed in the MgH$_2$ matrix (Fig. 5c). Such composite can release about 5 wt.% of hydrogen in 600 s at 573 K, with a significant improvement relative to unprocessed MgH$_2$. Further addition of catalyst and processing at higher intensity had a negligible effect on the hydrogen desorption kinetics indicating that a critical parameter is represented by the volume density of catalyzing particles and the corresponding average interparticle distance. In conclusion it results that, above a defined threshold, the density of catalyzing particles does not represent anymore the reaction rate limiting step so that different aspects of the reaction path have to be taken into account in order to further speed-up the desorption process.

So, in order to be able to point the most relevant factor, it is crucial to have a better understanding of the changes made by the ball milling treatment.
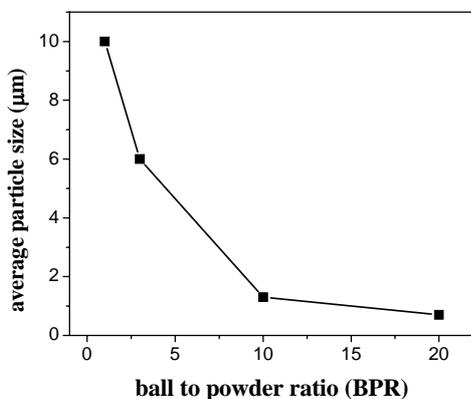
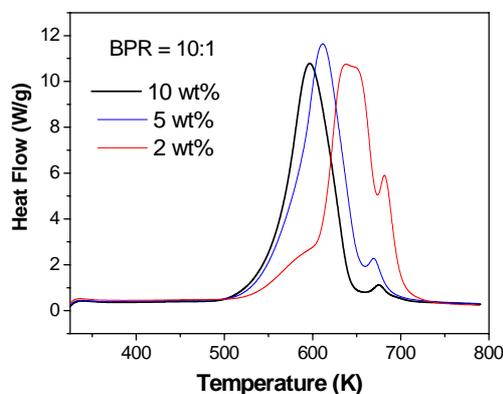Fig. 6. Average particle size of Co in MgH$_2$ - 10 wt.% Co samples milled at different BPR values [36]

Fig.7. DSC traces of MgH$_2$ – Fe composite [36]

Theoretical approach to hydrogen storage materials

A fundamental understanding of the hydrogen interaction in materials requires a synergistic approach involving both theory and experiment. Theory and computation can be used not only to understand experimental results, but also to guide them. The large advances in methodology (theory and algorithms) and increases in computational power in recent years have opened up new possibilities for theoretical studies of hydrogen storage.

Yu and Lam have studied the electronic and structural properties of MgH$_2$ using DFT [37]. Assuming the experimentally stable rutile structure of MgH$_2$ they minimized the total energy by optimizing the lattice parameters. The calculated equilibrium values agreed to within 2.2 % of the experimentally determined values. Analysis of the electronic properties shows that MgH$_2$ is an insulator with a band gap of 3.06 eV. However, this is 2 eV lower than the experimentally determined band gap. The cohesive energy is found to be 11.2-13.5 eV (exp. 13.56 eV). From this the enthalpy of formation of magnesium hydride is approximated to be between $\Delta H_f = -38,4$ kJ/mol H$_2$ to $\Delta H_f = -72$ kJ/mol H$_2$ (exp. $\Delta H_f \approx -75$ kJ/mol H$_2$). The discrepancy between theory and experiment may probably be assigned to the choice of the LDA (Local Density Approximation) exchange-correlation. First-principles electronic simulations can offer great insight into the understanding of the influence of alloying elements on the hydride properties. Song et al. has investigate the influence of Al, Ti, Fe, Ni, Cu on stability of MgH$_2$ by means of electronic structure and total energy calculations using the FP-LAPW method within the GGA. The influence of selected alloying elements on the stability of

MgH$_2$ was determined from the difference between the total energy of MgH$_2$-X and the total energies of the magnesium dihydride, the pure metals, and the hydrogen molecule [38]. Stier et al. [39] carried out various theoretical calculations based on density functional theory to study how binding energy and diffusivity of hydrogen change in magnesium hydride when other elements are added. The calculations make use of a plane wave basis set, ultrasoft pseudopotentials, the PW91 gradient dependent functional and the VASP code [40,41].
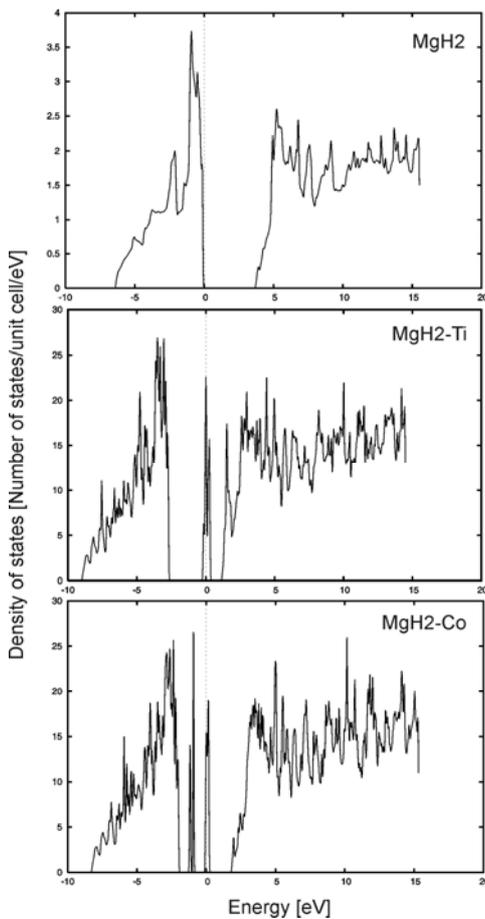

Fig 8. *Total DOS of MgH$_2$, MgH$_2$-Ti and MgH$_2$-Co systems[42]*

In our calculations of densities of states (DOS) [42] presented in Fig 8, for both MgH$_2$-Co and MgH$_2$-Ti composite systems we have found that high number of states at Fermi level implies stability weakening of overall compound in comparison with starting material (MgH$_2$). We have also found that heat of formation is not the only valid criterion for the best material for hydrogen storage.

Summary

The challenge is clear and fascinating: supplying more and more abundant and clean energy, consuming less and less natural resources and finding the appropriate solutions for any corner of the planet.

Fundamental theoretical and experimental research is needed to understand the interaction of hydrogen in solid-state materials in order to realize the potential of these materials for hydrogen storage.

The knowledge gained from this research will allow the tailored design and synthesis of new materials that will meet the requirements for efficient hydrogen storage.

Safety is a prime requirement for the success of the hydrogen economy. The development of predictive models for the dynamics of free H$_2$ in air in open and enclosed spaces would allow the assessment of risk and establishment of safety procedures for specific activities of

the hydrogen economy, such as hydrogen vehicle refueling, driving in partially enclosed tunnels, indoor parking, and vehicle repair. Models of hydrogen ignition and detonation in the presence of vapors from common volatile liquids would enable new standards for their use in proximity to hydrogen. Fundamental knowledge of hydrogen embrittlement of metals and welded joints would enable the setting of standards for the materials used in building a hydrogen infrastructure. Sensitive, selective sensors for detecting hydrogen would warn against the danger of fire or explosion in sheltered or enclosed areas.

References

[1]   A. Zuttel, Naturwissenschaften, 2004, 91 p. 157
[2]   L. Schlapbach, A. Zuuttel, Nature, 2001 414 p. 353
[3]   D.K. Ross, Vacuum 2006, 80, 1084
[4]   M. Bououdina, D. Grant, G.Walker, Int.J. Hydr. Energy 2006, 31,177
[5]   www.gm.com
[6]   www.bmwworld.com/hydrogen
[7]   www.diamlerchrysler.com
[8]   http:// world.hond.com
[9]   www.toyota.co.jp
[10] C.M. Jensen, R. Zidan, N. Mariels, A. Hee, C. Hagen, Int. J. Hyd. Energy 1999, 24 p. 461
[11] N Gerard, S. Ono, Hydrogen in Intermetallic Compounds II, 165. Springer (1992). editor L. Schlapbach.
[12]   M. C. V Sastri , B.Viswanathan, S. S. Murthy, Metal Hydrides. Springer-Verlag, Berlin, (1998).
[13] G.Sandrock, S.Suda, L. Schlapbach, Hydrogen in Intermetallic Compounds II, 197. Springer (1992). editor L. Schlapbach.
[14] A. Zaluska, L.Zaluski,   J. O. Strom-Olsen, J. Alloys Comp. 1999,288, p.217
[15] J. Bloch, M. H. Mintz, J. Alloys Comp. 253-254, 1997, p. 529
[16] M.Martin, C.Gommel, C. Borkhart, E. Fromm, J. Alloys. Comp. 1996, 238, p.193
[17] P. S. Rudman, J. Appl. Phys. 1979, 50, p. 7195
[18] Z. Luz, J. Genossar, P. S. Rudman, J. Less-Common Met. 1980, 73, p. 113
[19] L.Belkbir, E. Joly, N. Gerard, Int. J. Hydr. En. 1981, 6, p.285
[20] B. Vigeholm, K. Jensen, B. L., Pedersen, A. S. J. Less-Common Met. 1987, 131, p. 133.
[21] V. P. Zhdanov, A. Krozer, B. Kasemo, Phys. Rev. B 47, 1993, p.11044
[22] K. B. Gerasimov, E. Y. Ivanov, Mat. Lett. 1985, 3, p.497
[23] K. B. Gerasimov, E. L. Goldberg, E. Y. Ivanov, J. Less-Common Met. 1987, 131, p. 99
[24] M. H. Mintz, Z. Gavra, Z. Hadari, J. Inorg. Nucl. Chem. 1978, 40, p.765.
[25] L. Zaluski, A. Zaluska, J. O.Strom-Olsen, J. Alloys Comp. 1997, 253-254, p.70
[26] J. Huot, G. Liang, S. Boily, A. V. Neste R. Schulz, J. Alloys Comp. 1999, 293-295, p. 495
[27] W.Oelerich, T.Klassen, R.Bormann: J. Alloys Comp. 2001, 315, p.237

[28] A. Zaluska, L. Zaluski, J.O. Ström-Olsen: Appl. Phys. A, 2001, 72 p. 157

[29] A. Ming, Mat. Sci. Engineering B 2005, 117 p. 37

[30] G. Liang, J. Huot, S. Boily, A. Van Neste, R. Schulz, J. Alloys Comp. 2000,297, p. 261

[31] J. Hout, G. Liang, R. Schulz, App. Phys.A, 2001, 72, p.187

[32] L. Zaluski, A. Zaluska, J.O. Ström-Olsen, R. Schulz, J. Alloys Comp. 1995, 217, p. 295

[33] J-L. Bobet, E. Akiba, Y. Nakamura, B. Darriet: Int. J. Hyd. Energy ,2000,25 p.987

[34] O. Gutfleisch, S. Dal Toè, M. Herrich, A. Handstein, A. Pratt, J. Alloys Comp. 2005, 404-406, p. 413

[35] A. Basseti, E. Bonetti, L. Pasquini, A. Montone, J. Grbovic, M. Vittori Antisari: Eur. Phys. J. B 2005, 43, p. 19

[36] A. Montone, J. Grbovic, Lj. Stamenkovic, A. L. Fiorini, L. Pasquini, E. Bonetti, M. Vittori Antisari: Mater. Sci. Forum 2006, 518, p.79

[37] R. Yu, P. K. Lam, B 1988,37, p.8730.

[38] Y. Song, Z. X. Guo, R. Yang, Phys. Rev B 2004, 69, p. 094205

[39] W. Stier, L.Gabriel Camargo, F.Óskarsson H. Jónsson ,Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem. 2005, 50 (1), p. 15

[40] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J., Singh, C. Fiolhais, Phys. Rev. B, 1992, *46*, p.6671.

[41] G. Kresse and J. Hafner, *Phys. Rev. B* 1993, *47*, p.558.

[42] J.Grbović Novaković T. Brdarić, N.Novaković, Lj.Matović, A. Montone, S. Mentus, Experimental and Theoretical Investigation of Hydrogen Storage in Magnesium Based Composites, submitted to Mat.Sci.Forum, 2006