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Hydrogen production by hydrolysis from Mg rich compounds and composites NdNiMg₁₅-Mg : How to combine fundamental and applied science?

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Abstract

Composites materials Mg-NdNiMg₁₅ can be easily obtained by directly melting pure elements. Young modulus and hardness can be varied from 43.5 to 48.8 GPa and 45 to 225 HV respectively. Nevertheless, the corrosion resistance of these composites is really poor, preventing a potential structural application. The use of composites Mg-NdNiMg₁₅ for the production of hydrogen through hydrolysis is therefore obvious. The design of a prototype allowing to produce hydrogen from hydrolysis of a patented magnesium-based powder is described. The Life Cycle Analysis highlights that the presence of Ni (to favor the galvanic coupling and therefore the hydrolysis reaction) in the powder is the main drawback of this solution (especially in term of human health and resources). The use of Mg-NdNiMg₁₅ composites allows to divide up to 2 the content of Ni compared to the patented powder and also remove the ball milling in the fabrication process. As such, it is a way to combine fundamental (new compounds, new structure) with applied science (prototype and *in situ* generation of hydrogen).

Key words : Hydrolysis, light mobility, structural analysis, green hydrogen, Life Cycle Analysis

Introduction

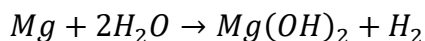
It is now admitted that the fossil fuel consumption has to decrease because of its rarefaction, its rising cost and its impact on the environment. Nevertheless, most of the renewable sources of energy are intermittent and thus an energy buffer is needed. Hydrogen often appears as the best energy vector as it can store large quantity of energy and its combustion is clean (no CO₂ emission, only H₂O emission). Many difficulties have to be overcome for a large-scale use of Hydrogen: the production, the transport and the storage (and according to some authors, the use too). In fact, hydrogen is mainly produced from fossil fuel (which does not solve the issue of fossil fuel usage) and the storage is mainly done under pressure. Efforts are mainly oriented towards improving the production of clean hydrogen (by electrolysis with renewable electricity) and storage density (metal hydrides often appear as a good solution for stationary storage)[1-2].

During the past 50 years, magnesium rich compounds have attracted a lot of interest in the field of material science for both fundamental crystal chemistry [3-4] and also for interesting properties (*e.g.* corrosion resistance compounds within the Mg-T-RE ternary (RE: Rare Earth, T = Transition metal [5-7])). Recently, many studies were dedicated to the (re)investigation of the Mg-rich part of the RE-T-Mg diagrams to find new compounds for fundamental research and if possible for solid hydrogen storage. Magnesium is a very interesting candidate as it offers a high reversible gravimetric capacity (*i.e.* 7.6%) for solid hydrogen storage. However, a poor hydrogen sorption kinetics and a high operating temperature limit its application[8]. The goal of looking for new Mg-rich compounds was to change

the thermodynamic of the sorption reaction by changing the chemical bond scheme. As binary compounds have been known for a long time, most recent studies focus on ternary compounds. Increasing the amount of magnesium (i.e by staying close to the Mg-corner of the ternary diagrams RE-T-Mg) will reduce the density of the material (which will increase the gravimetric energy density for hydrogen storage) and its cost. As examples of Mg-rich phases (the lightest ones), we can name: LaCuMg₈ [9], Gd₁₃Ni₉Mg₇₈ [10], La(Ag_{1.37}Mg_{10.63}) [11], Ce₂Ru₄Mg₁₇ [12], NdNiMg₅ [13], Nd₄Ni₈Mg₈₀ [14], Nd₁₆Mg₉₆Ni₁₂ [15], NdNiMg₁₅ [16]. The studies of hydrogen sorption properties [14-15, 17-18] showed a decomposition of the ternary phase into binary and ternary hydrides after the first hydrogen absorption. Nevertheless, some of the mixtures obtained after the decomposition show good hydriding/dehydriding properties. This is mainly due to the close mixtures between the various components induced by the chemical decomposition (e.g. some authors named it “chemical milling” as the results can be as good as the ones obtained from ball milling for a long time).

Another interest of the use of magnesium is the development of lightweight materials. In this field, the new ternary phases called LPSO (Long Period Stacking Ordered) have been discovered and some of them have been structurally characterized such as Mg₃₀Co₂Y₉ [19] and Y₄Zn₃Mg₂₃₋₃₅, [20]. This is a very good example of a combination of fundamental and applicative research. Hydrogen sorption properties of alloys containing LPSO phases as well as hydrolysis performances were also studied [21-23].

For the past 15 years, efforts have been dedicated to the hydrolysis process which consists in using water as an hydrogen source. The water is reduced by a metal or an alloy into hydrogen and HO⁻ ions. It would solve both the production and the storage issues as the hydrogen can be produced on demand. Such process requires a light and cheap element and magnesium appears as the best element to be used [24-25]. The hydrolysis reaction can be written as follows:



Such solution offers low security concerns as hydrogen is produced *in situ*, no storage is needed and the byproduct Mg(OH)₂ is innocuous. 1L of hydrogen can be produced with 1 g of magnesium. A lot of studies already demonstrated that it is possible to use magnesium scraps alloys [26] instead of pure magnesium even if magnesium alloys are designed to have a better corrosion resistance [27-29]. Using MgH₂ can appear to be an excellent solution as the production of hydrogen will be twice as important. However, in terms of material cost, the use of magnesium is much more economical (average cost of Mg is 2 to 4 €/kg as it is 20 to 50 €/kg for MgH₂).

Nevertheless, all solutions have disadvantages. The main one with hydrolysis is the reversibility of the reaction. In fact, going back to Mg from Mg(OH)₂ will require a huge quantity of energy (more or less 10 times the energy produced by the hydrogen generated). That could make this alternative non-viable for extensive applications but, considering the valorization of magnesium alloys waste, this solution is very promising, especially for small portable/mobile applications.

The main idea of the paper is to start from a defined compound, then to make a composite very rich in magnesium with this defined compound then finally, to look at the various possible applications (hydrogen storage, structural applications, hydrolysis,...). After briefly describing the synthesis and

structure of composites Mg-NdNiMg₁₅, we will present the mechanical properties of such composites. Then, the hydrolysis behaviour as a function of the microstructure will be discussed. After, the Cycle Life Analysis of the product used to generate hydrogen will be presented. To finish, the application of such composites to produce hydrogen powering an electrically assisted bike will be presented.

Experimental details

The NdNiMg₁₅ and the Mg-NdNiMg₁₅ composites samples (containing a total of 70, 80 and 90wt.% of magnesium) were prepared by induction melting using neodymium pieces, nickel rods, and magnesium rods (all purities higher than 99.8%) as starting materials. To avoid oxide impurities, the surfaces of the magnesium and neodymium pieces were cleaned with abrasive tools in a glove box. Elemental pieces were then appropriately weighed and sealed in tantalum ampoules under an argon pressure of ca. 800 mbar. The argon was purified before with magnesium sponge (673 K). The ampoules were heated with a high-frequency furnace at approximately 1773 K and kept at that temperature for 2 min before turning off the furnace. This corresponds to the so-called as-cast samples. For annealed samples, the tantalum ampoules were placed in an evacuated quartz tube for a subsequent annealing at 823 K or 973 K for 7 days. The temperature was then decreased to 300 K at a controlled rate of 6 K/h (in order to remain as close as possible to the thermodynamic equilibrium).

For the preparation of the patented powder used as reference in this paper (*cf.* b) and c) in Results and Discussion section) Mg-Ni(5wt.%)–C (5wt.%), more details can be found in ref [30]). The magnesium powder metal was ball milled with a Fritsch P5 miller with addition of graphite powder and nickel powder. Powder was passed through a sieve of 200 µm and sometimes sieved again to 100 µm and stored in a glove box filled with purified argon.

SEM observations were made using a TESCAN VEGA3 SB and SERON TECHNOLOGY microscope equipped with Secondary Electron and Back Scattered Electron detectors (hereafter referred to as SE and BSE modes respectively). Furthermore, the elemental composition of the surface was estimated using EDX spectrometer.

For the microhardness, a Leica VMHT (auto) has been used with a standard diamond pyramid indenter with a square base and an angle at the top between the opposite faces equal to 136°. The force and duration of the pressure are respectively 100 N and 10 sec for our measurements. For the determination of the Young modulus, a homemade apparatus (Limoges University) based on ultrasonic reflection method at 10 MHz was used.

The hydrolysis performances of the materials were evaluated by monitoring the volume of hydrogen produced over time in a 3.5 wt.% NaCl aqueous solution (*i.e.* similar to seawater) [31-34]. Hydrogen production is presented as the conversion yield (%), which is defined as the volume of produced hydrogen over the maximum volume of hydrogen measured after acid addition (which

corresponds to the theoretical value calculated using the hydrolysis equation of pure Mg [35]). The tests were made at least three times to ensure repeatability.

The other details on the experimental part can be found in the references cited in the text.

Results and discussion

a – Nd-Ni-Mg system and the composites Mg-NdNiMg₁₅

Recent investigations (from 2013 to 2018) of the Nd-Ni-Mg ternary diagram around the Mg-corner have shown the existence of four new compounds [13-16], they are reported in figure 1a. Two of them, Nd₄Ni₈Mg₈₀ and NdNiMg₁₅ are, to our knowledge, the Mg-richest ordered ternary compounds ever reported. Hydrogen storage properties of these new Mg-rich phases were studied [14, 15, 17]. Despite the decomposition observed after the first hydrogenation, the hydrogen sorption reactions exhibit very good kinetics and high storage capacities (more than 3 wt.%).

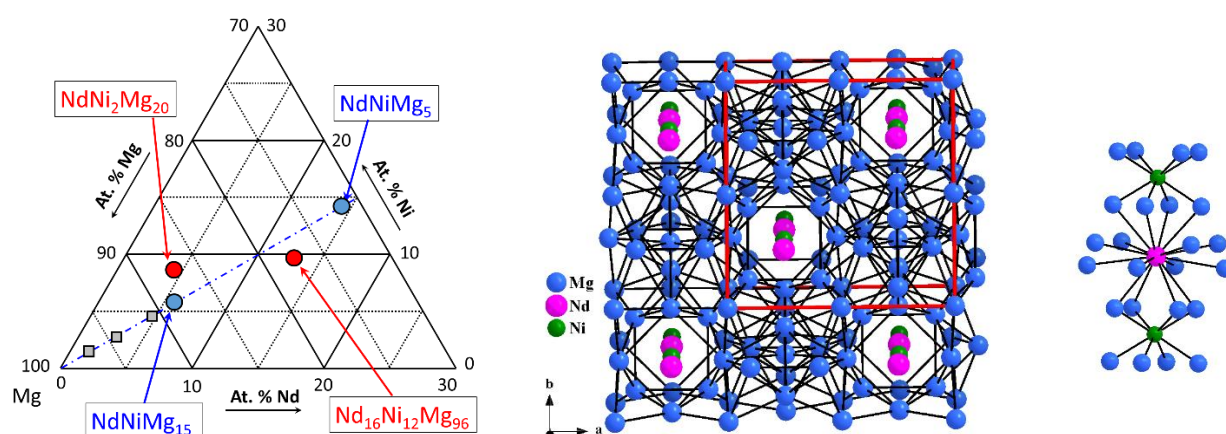


Figure 1. : (a) ternary Nd-Ni-Mg diagram showing the Mg-rich phases recently discovered. The squares correspond to the composites studied in the following sections. (b) Crystal structure of NdNiMg₁₅

The richest Mg ternary compound discovered during the last 20 years, NdNiMg₁₅, is very interesting from a fundamental point of view. It crystallizes with a new ternary ordered variant of the V₁₅Sb₁₈ structural type (SG P4/nmm; a = 10.0602 Å and c = 7.7612 Å). The structure is presented in figure 1b. Basically, it can be described as a Mg matrix with some lines of Nd-Ni. The 3D network of magnesium atoms is made of Mg₄ tetrahedra sharing faces or edges, with Mg–Mg distances ranging from 2.944 to 3.451 which are consistent with the value of 3.2 Å observed in Mg metal. The distances Nd-Ni within the chains are equal to 3.858 and 3.903 Å which is far from the sum of the metallic radius (about 3.05Å). That means that only weak chemical bonds may exist between Nd and Ni and that the bonding is done through the magnesium atoms (figure 1b on the right). The structure is fully described in ref [16]. It has been shown that this compound displays an antiferromagnetic transition at T_N = 9K and that only the Nd is magnetic (i.e. μ_{eff} = 3.58 μ_B as the theoretical value for Nd is 3.62μ_B). In addition, a metamagnetic behavior appears at T < 9K. This shows that such compound can have very interesting physical properties.

Also, the question of the existence and the stability of composites Mg-NdNiMg₁₅ must be asked. In order to answer, we elaborated composites with various amounts of reinforcement (NdNiMg₁₅ compound) ranging from 0 to 100%.

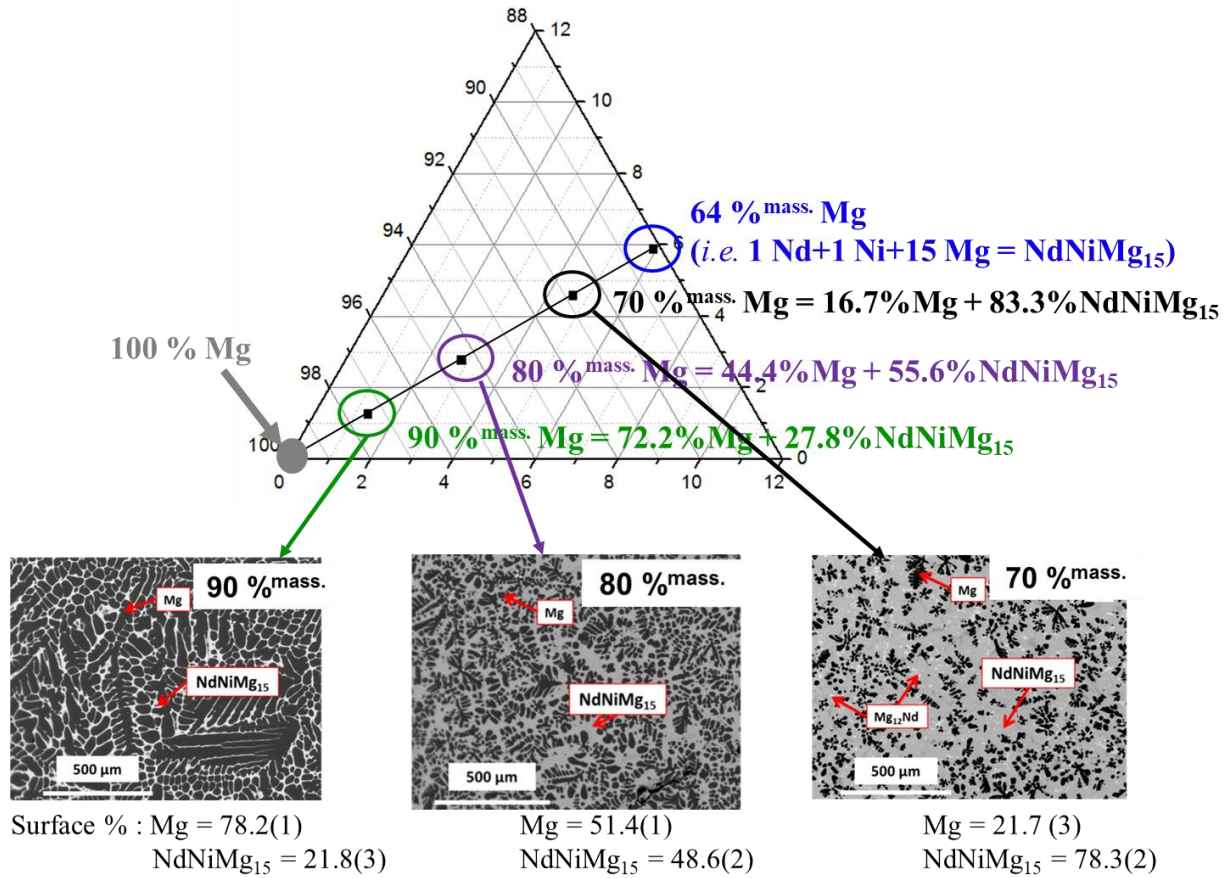


Figure 2 : SEM (BSE) of composite materials Mg+NdNiMg₁₅ with the location on the Gibbs triangle [36]. The surface % was calculated with ImageJ software using 10 different SEM observations

As shown from the SEM analysis presented on figure 2, it is possible to directly create the composites Mg-NdNiMg₁₅ (thus containing a total of 70, 80 or 90 wt.% of magnesium) by melting the appropriate amount of the three chemical elements Ni, Nd and Mg. On the SEM (BSE) images, Mg appears as black and the reinforcement NdNiMg₁₅ appears as light grey. These results confirm that NdNiMg₁₅ is the richest phase in magnesium. The distribution of the reinforcement is rather homogeneous whatever the relative amount in the composite. It is worth pointing out that magnesium appears as dendrites. It was expected as the composite is directly obtained by melting of the elements without any post thermal treatment.

An obvious property is the lightness of NdNiMg₁₅ with a density of 2400 kg/m³ and therefore it can be interesting for structural applications. In addition, the compound NdNiMg₁₅ exhibits a microhardness of 225 vickers while it is only 45 for magnesium. The Young modulus is also higher than the one of magnesium (48.8 GPa against 43.5 GPa, respectively). The rather small variation of the

Young modulus between NdNiMg₁₅ and Mg can be explained by the difference in chemical bonds between the two compounds. In fact, as described earlier, in NdNiMg₁₅, most of the bonds are Mg-Mg ones (*i.e.* like in metallic Mg) and only weak Nd-Ni interactions may exist. This will lead to a small variation of the Young modulus. In the case of microhardness, the microstructure also plays an important role in explaining the huge difference (a factor of almost 5).

For that purpose, the mechanical properties of the composites Mg-NdNiMg₁₅ (thus presented in figure 2) were studied. As presented in table 1, it follows a mixture law. The Young modulus increases from 43.5 to 48.8GPa with increasing the amount of reinforcement (*i.e.* NdNiMg₁₅). The microhardness increases from 45 to 225 HV. Therefore, it is possible to adjust the mechanical properties by adjusting the amount of reinforcement. Such adaptive materials can be of prime importance considering also the very low density (*i.e.* about 2000 kg/m³) of the composite material.

Table 1 : Mechanical properties of the various composites elaborated with a relative weight % of NdNiMg₁₅ reinforcement ranging from 100 to 0% (meaning a total wt.% of Mg within the composite ranging from 64 to 100%) [36].

Wt% of reinforcement (<i>i.e.</i> NdNiMg ₁₅)	Wt% of matrix (<i>i.e.</i> Mg)	Total wt% of Mg within the composite	Young Modulus E (GPa)	Microhardness (Vickers)
100	0	64	48.8	225
83.3	16.7	70	47.3	200
55.6	44.4	80	46.1	138
27.8	72.2	90	44.5	84
0	100	100	43.5	45

The effect of annealing was also studied by comparing as-cast samples and annealed ones at 550°C and 700°C. These annealing temperatures were chosen because they are on either side of the melting temperature of the composites (around 600°C). Annealing at 700°C leads to a remarkable increase in the size of the Mg grains, with still the presence of the NdNiMg₁₅ phase (confirmed by microprobe analysis) at the inter-granular zone. Annealing at 550°C, leads to a precipitation of this phase (*i.e.* NdNiMg₁₅) inside the Mg grains. The presence of small precipitated phases inside the Mg grains results from being at a temperature below the melting temperature. On the other hand, when the temperature is increased up to 700°C, we then witness a dissolution of the precipitates, but upon cooling the NdNiMg₁₅ crystals created at the melting temperature become stable which initiates their germination and growth at the Mg grain boundaries.

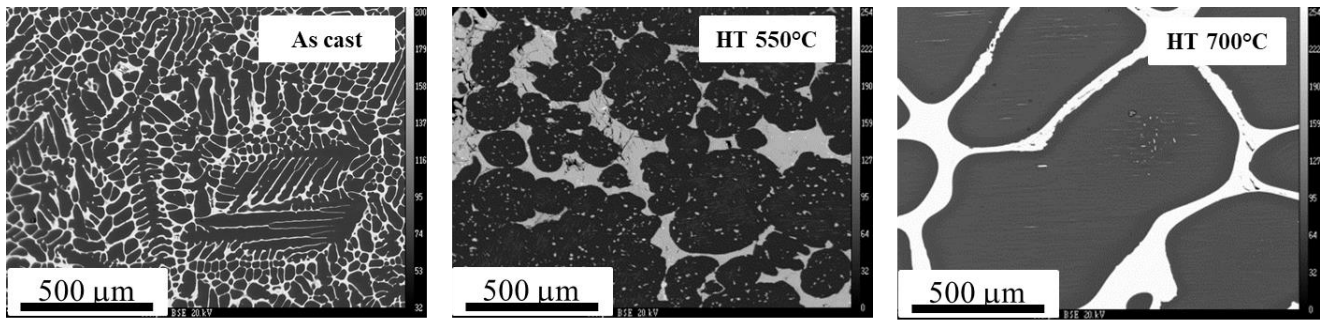


Figure 3 : SEM of composite materials $Mg+NdNiMg_{15}$ containing 90wt.%Mg (i.e. 78% of $NdNiMg_{15}$ and 22% of Mg) with different heat treatment (i.e. as cast, heat treated at 550 and 700°C with a cooling rate of 6°C/h).

Therefore, it is also possible to adjust the microstructure and so the mechanical properties and playing on the thermal treatment. Nevertheless, to be as cheap as possible, it will be better to avoid any thermal treatment.

b – Design of a prototype

The prototype designed for the production of hydrogen from magnesium (and alloys and other metals) is presented in figure 4. It is worth pointing out that this prototype is not optimized in term of weight and volume. Nevertheless, it consists of stainless steel material, the water content is 2 L, the maximum Mg (or alloys) content in the capsule is 100 g and the total weight of the system is 6 kg.

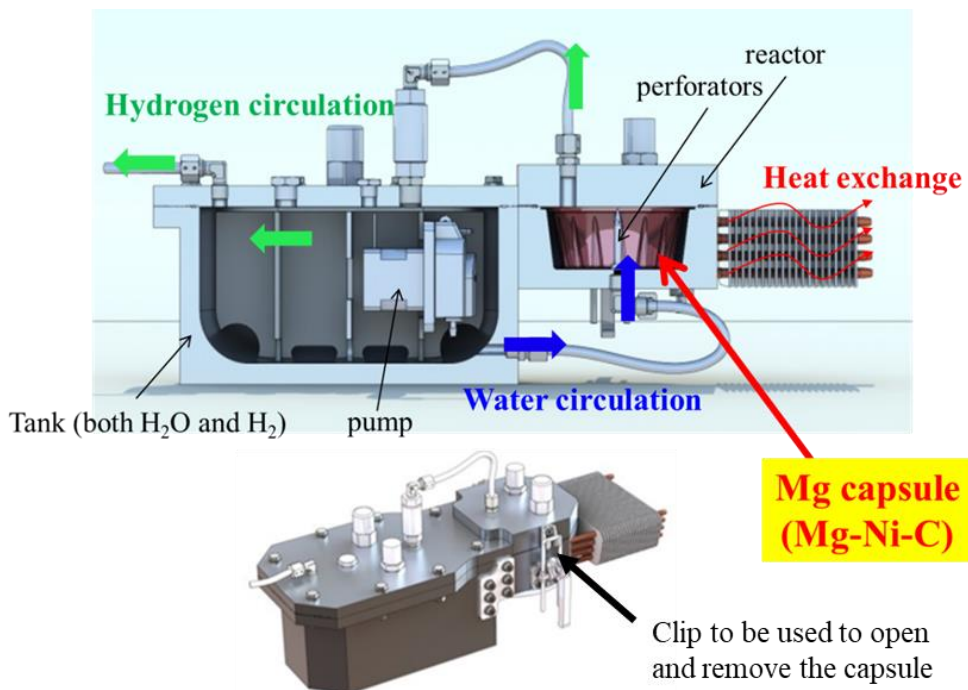


Figure 4 : Scheme of the H_2 delivery system

When hydrogen is needed, water is injected on the capsule containing the Mg powder by a peristaltic pump. Then the reaction of hydrolysis occurred and hydrogen is produced within a delay of

maximum 1 second. As the reaction is strongly exothermic, a heat exchanger has been added close to the reactor. The hydrogen produced can be either stored above the water in the small tank or directly use by a fuel cell linked to the prototype. If no more hydrogen is needed, the water circulation is stopped and the reaction stops instantaneously. The reaction can start again so that the production of hydrogen can be considered as “on demand”. Command laws have been established and allowed to control the flux and the pressure of hydrogen [37]. When all the magnesium is consumed (*i.e.* transformed in $\text{Mg}(\text{OH})_2$), the reaction stopped and the capsule has to be renewed. With the clips system (low part of the figure 4) it is an easy process taking less than 1 minute. With a small capsule of 100 g (considering that the mixture is composed of 90% of Mg and 5+5 % of additives like Ni and C [30]) it will produce 87 L of hydrogen with an energy of 902 kJ. It corresponds to (considering a yield for the fuel cell of 50%) 125W.h which is sufficient to provide enough energy for an electrical assisted bike (usually ranging from 100 to 150 W.h).

The response time is very short as the reaction is instantaneous. It takes less than 1 second for the hydrogen to start being produced and less than 2.5 seconds to reach a flow rate of 3.5L/minute which is the minimum acceptable flow rate for the fuel cell (Cf supplementary materials, figS1 a and b). Thus, the control of the water flow (control box and associated control law) allows to control and to adjust the hydrogen flow. By setting a pressure of 2.5 bars of hydrogen at the outlet of the hydrolysis reactor, it is possible to adjust the power of the cell according to the user's demand. Thus, it is shown (Cf supplementary materials, fig S2) that it is possible to adjust the power produced between 0 and 84 watt during a little more than 5 minutes (with 15 g of magnesium).

Thus, for 100g of magnesium, depending on the power supplied by the user and on the riding speed, it is possible to travel between 1.5 and 6 km (Cf supplementary materials, table S1). Thus the autonomy of the prototype in the bike can be estimated between 15 to 60 km/kg Mg. The energy density of the prototype is weak (120 Wh/kg system and 280Wh/L system) because it has been designed for laboratory use (numerous measuring sensors have been added) and it has been designed to withstand pressures of up to 100 bar (whereas the working pressure is 2.5 bar maximum). Thus, it is possible to considerably lighten the system.

Therefore, in order to test it in real condition, the prototype was installed on a bike (Figure 5). The fuel cell (Horizon®, 100W) was connected to the prototype and the electric motor (12V DC) from Jadeshay (brushless type, ref BZN-27730425, maximum output power of 150W) was powered. With this non-optimized system, it was possible to prove that the system is working and robust enough. The bike has been running for 100km in total by step of 1 to 3 kilometers only (as the powders are still produced at the laboratory level; private tests only) and various user tested the capsule change with success.

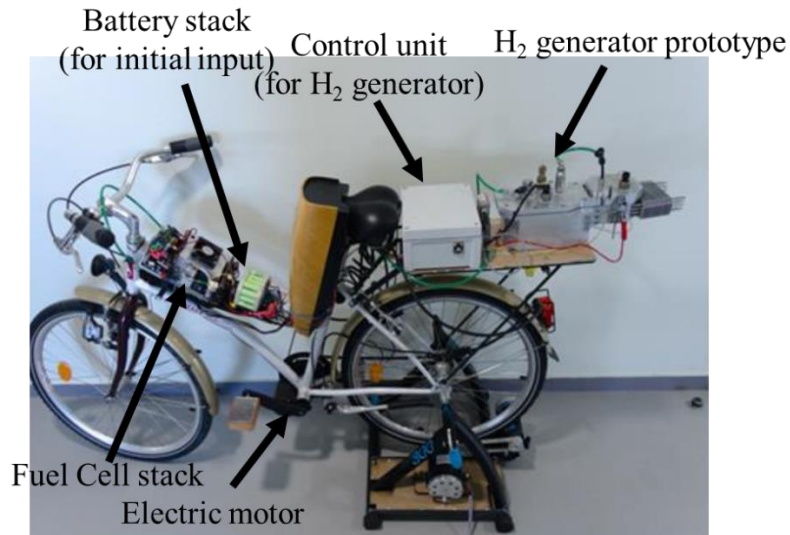


Figure 5 : the E bike to evaluate the efficiency and autonomy allowed in real situations.

c – Life cycle analysis of the capsule (used in b)

Nowadays, it is not possible to design a new setup without considering the LCA (Life Cycle Analysis). This becomes a critical point for all the new materials and systems. The endpoints (area of protection) were used rather than the midpoints just to give a more global overview. Each endpoints include several midpoints which are as follow:

Human health : human toxicity (cancer and non cancer effects), particulate matter, ionizing radiation, ozone formation, climat change.

Ecosystems : climate change, ecotoxicity, acidification, terrestrial and marine eutrophication, freshwater eutrophication and ecotoxicology.

Resources : land use, water resources depletion, mineral and fossil resources depletion.

Global warming : climate change, ozone depletion

Only the impact of the processing of the capsule was taken into account. Details about the methodology used here can be found in reference [38] and [39]. The recycle of the end product (*i.e.* $Mg(OH)_2$) is not considered. Results are presented on figure 6.

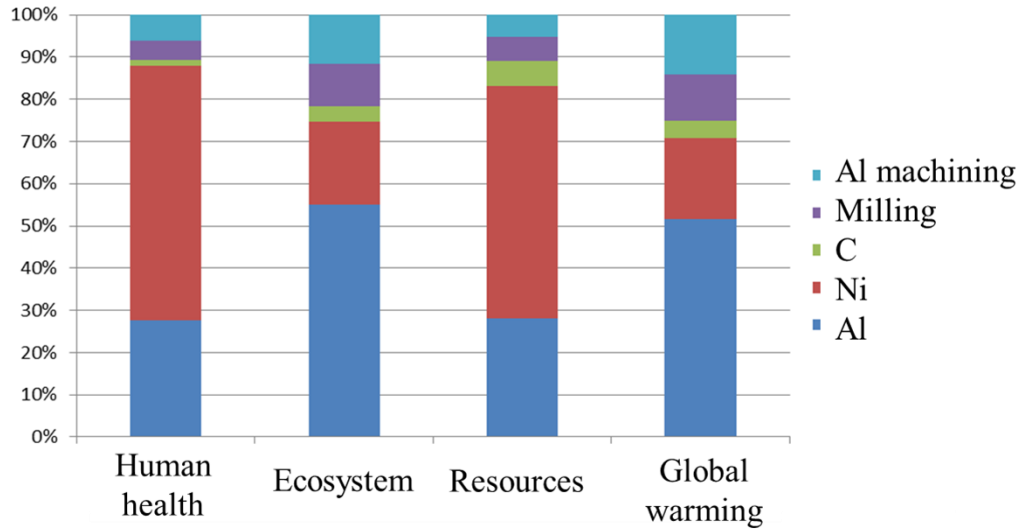


Figure 6 : Life Cycle Analysis ; Impact of the processing of the capsule

From this figure it is clear that for the 4 points considered, the Nickel (added to enhance the corrosion by creating galvanic coupling between Mg and Ni) and the Aluminium of the capsule are the crucial points. It is especially true for the human health and the resources (as Ni is considered as a critical material). All the other factors: Al machining, C addition, milling process, etc. have a very low impact on the 4 considered points. The case of aluminium can be easily solved by using recycled aluminium instead of fresh one. Doing that will lead to an almost null contribution of aluminium in the LCA. Therefore, it leaves us with the problem of Ni that has to be solved. Other metals were tried but the galvanic coupling was always lower than with Ni.

It is also interesting to compare the hydrolysis process with the most frequently used process: the methane steam reforming. Results are shown in supplementary material (fig S3) and it is clear that if Ni is taken into account, the hydrolysis process is better considering the ecosystems and the global warming. This result was expected as the hydrolysis process does not emit greenhouse gases and allows to offer a second life to non-recycled magnesium alloys. Therefore, as the Ni impact is huge for both the human health and the resource, the hydrolysis process is slightly worse than the methane steam reforming, which is a surprising result. Nevertheless, if Ni is not taken into account, the hydrolysis process is better than steam reforming on all the 4 end points. The impact of hydrolysis is between one third and one half that of the steam reforming. This last result clearly highlights that the replacement of Ni is of prime importance.

d – Hydrolysis properties (duality solid state chemistry/application)

The composite materials presented in section (a) highlight the possibility of using them as structural material. Nevertheless, if the mechanical properties can be adjusted and can be as good as the ones of Al and Mg alloys, another important point has to be considered: the corrosion resistance. For that purpose, the composite materials were immersed into water (salted water to accelerate the

corrosion). This results instantaneously in the formation of bubbles on the surface of the composites. After 20 minutes, the composites were almost fully consumed (Cf inset in figure 7). It has been determined by chromatography and mass spectra that the bubbles consist of hydrogen. Therefore, it must be concluded that the composite cannot be used as structural material as expected. Nevertheless, the high reactivity of the composite towards water can be an excellent point for the generation of hydrogen by hydrolysis.

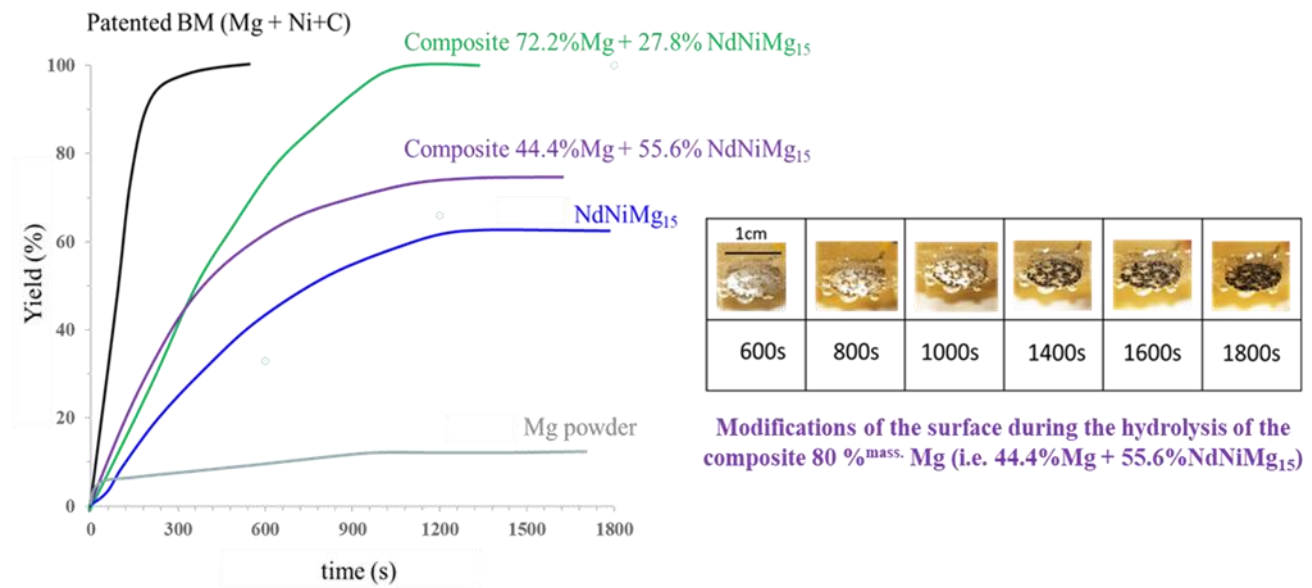
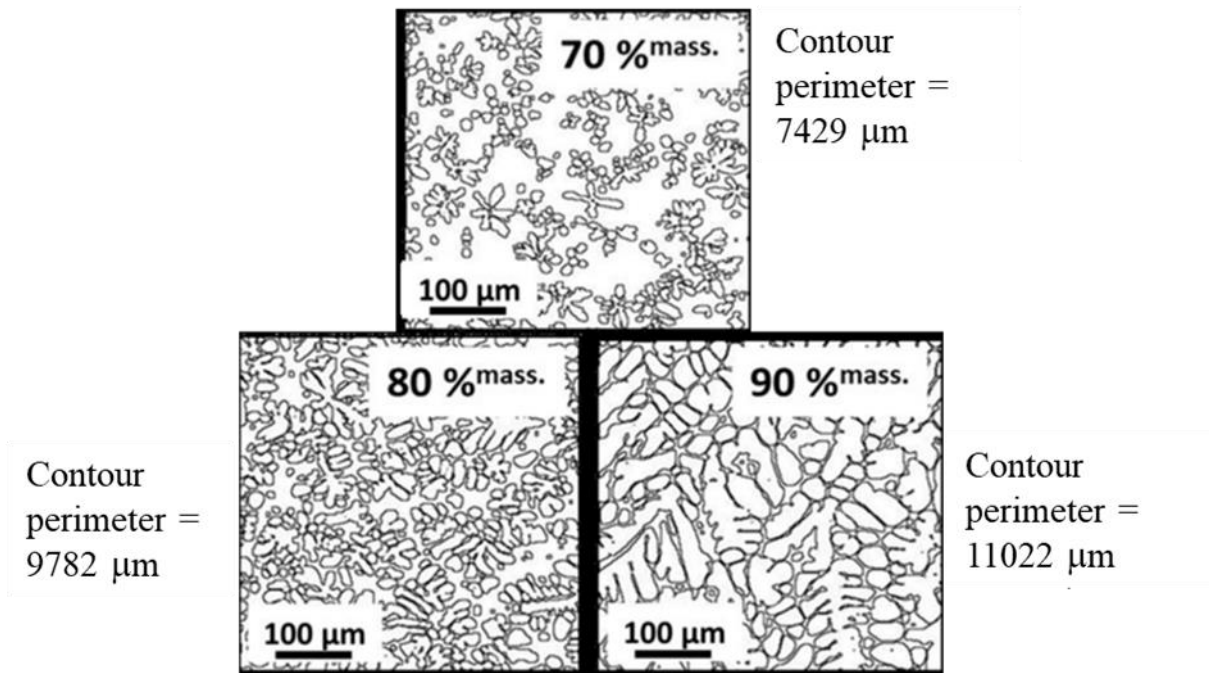


Figure 7 : hydrolysis behavior of various composite materials compared to optimized Mg+5%Ni + 5%C ball milled powder.

As shown on figure 7, the corrosion resistance of NdNiMg₁₅ is already lower than the one of Mg, therefore, the production of hydrogen is higher. Looking at the composite behavior, the situation, in term of corrosion is worse (e.g. mainly pitting and galvanic corrosion is observed) which means that the production of hydrogen is higher than for pure NdNiMg₁₅. In order to better understand the improvements of the hydrogen generation when the amount of reinforcement in the composites decreases, the contact between Mg and NdNiMg₁₅ was estimated by image analysis of SEM observations. The results are presented in figure 8.



Figure

8 : SEM micrographs of the microstructures processed by the ImageJ software which show the contact contours between the anodic and cathodic phases (NdNiMg_{15} and Mg) [36]. Values of the contour perimeter are given (accuracy is given in the text below).

The measurement of the perimeter of the contours (Figure 7) show that the contact zone increases with the increase in the proportion of the Mg phase. It has been estimated to 7429 (215), 9782 (236) and 11022 (515) μm for the composites at 70, 80 and 90 wt% in Mg, respectively. The improved hydrolysis performance of the composites and in particular for the 90wt.% Mg, therefore seem to be essentially associated with their microstructures. There is therefore better galvanic corrosion at the scale of the microstructure due to the better contact between the anodic phase (Mg) and the cathodic phase (NdNiMg_{15}).

The composite containing a total of 90wt.% of Mg allows to reach a complete reaction (100%yield) in less than 20 minutes. Such result should be compared with one of the best results obtained with a mixture of Mg+5wt.%Ni + 5wt.%C (the one patented and reported in the part b for the LCA). The kinetic is of course 4 to 5 times weaker for the composite but we were using bulk material and not powders (so, no ball milling have to be used). Our bulk sample will be easier to handle and safer to store than Mg rich powder mixture. To the best of our knowledge it is the best kinetic reported for bulk material up to now.

Coming back to the LCA presented in part c, it was shown that one thing to be solved was the presence of Ni. In the case of the composite material, the Ni is in the reinforcement NdNiMg_{15} so that means that the total amount of Ni is much lower than in the Mg+5wt.%Ni+5wt.%C patented powder (*i.e.* the amount of Ni in NdNiMg_{15} is only about 10wt.% which means that in the composite Mg- NdNiMg_{15} containing 90wt.% of magnesium in total, the total amount of Ni is reduced to 2.5wt.%). Then, the impact of Ni on the LCA will be reduce by a factor of around 2.

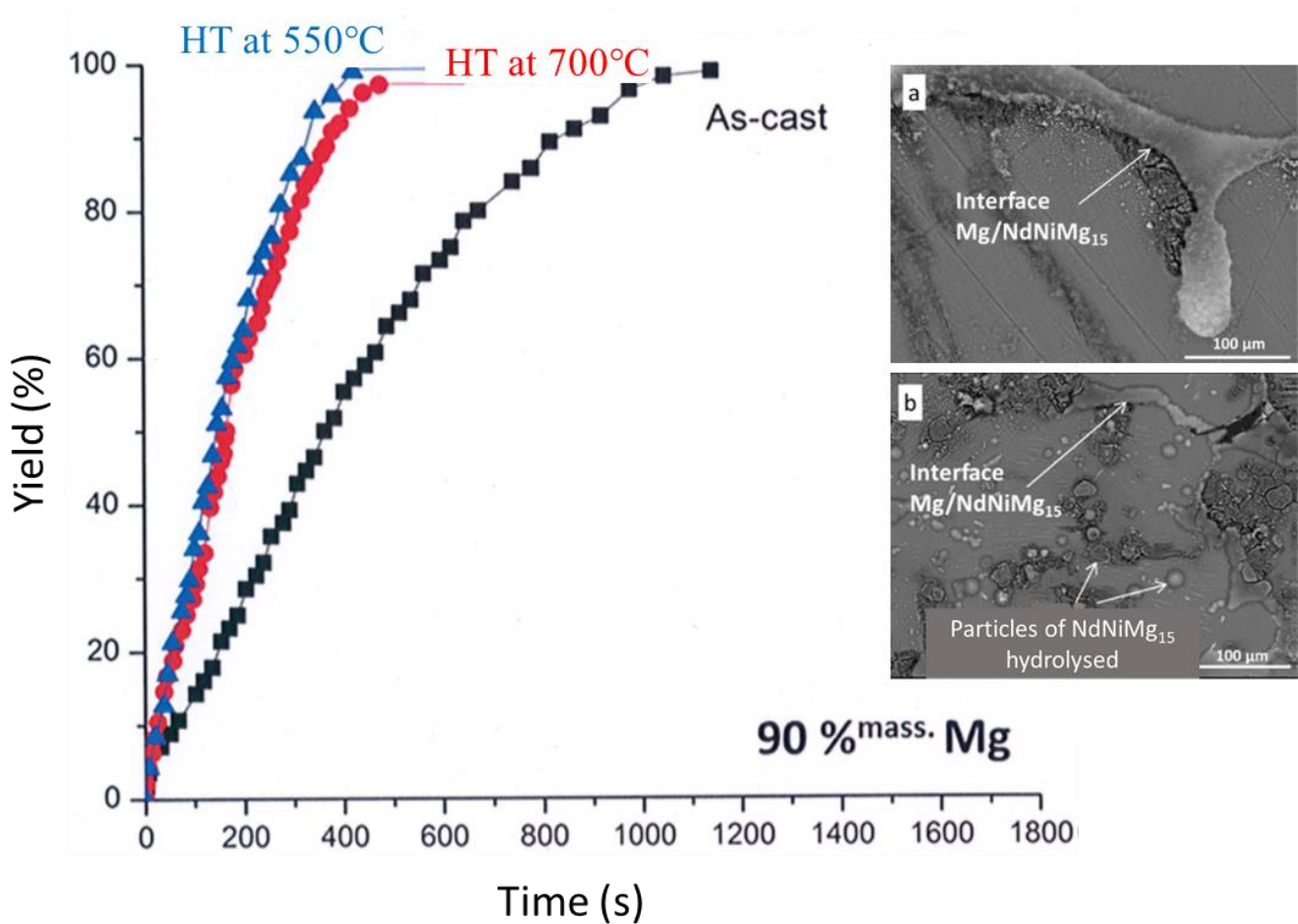


Figure 9 : hydrolysis behavior of the composites with 90% of Mg submitted to various heat treatment. SEM micrographies after 1 min immersion in salted water (35 g/L) for the composites heat treated at 700°C (a) and 550°C (b) are also presented.

Compared to the as cast composite with 90wt.% of Mg, composites annealed at 550 and 700°C also show a yield of 100% but with improved kinetics. About 400 seconds are needed to generate all the hydrogen, whereas only 55% of the theoretical yield is achieved for the “as-cast” composite for the same duration. SEM micrographs of the microstructure after 1 minute of hydrolysis were taken (Figure 9). In the case of the composites with 90wt.% of Mg annealed at 700°C, the presence of the NdNiMg₁₅ phase at the Mg grain boundary allows galvanic and intergranular corrosion at the Mg-NdNiMg₁₅ interface (figure 9). While in the case of the composite annealed at 550°C, the NdNiMg₁₅ phase is not only found in the intergranular zone but also in the form of particles inside the Mg phase. As corrosion progresses, these particles come into contact with water and become a galvanic corrosion site, which will allow corrosion to occur throughout the material. The increase in the size of the Mg grains and the presence of the NdNiMg₁₅ particles inside the Mg matrix improved the kinetics of the hydrolysis reaction of the composite considered.

Therefore, such composites materials, with or without heat treatment can be used to generate hydrogen. Such materials avoid the long and costly ball milling process usually required. It also allow to reduce a little the amount of Nickel within the mixture.

Conclusion

The study of the mechanical properties of rich Mg compound (i.e. NdNiMg₁₅) reveals that the Young modulus is 10% higher than that of Mg and the microhardness, because of the specific microstructure, is increased by a factor of 4 (compared to Mg). Composites Mg-NdNiMg₁₅ were prepared by direct melting of the three elements. The mechanical properties follow a mixture law with Young modulus varying from 43.5 to 48.5 GPa and microhardness from 45 to 225 Vickers. Nevertheless, it is also demonstrated that the corrosion resistance is very poor.

A prototype was presented for the production of hydrogen by hydrolysis of magnesium. It was demonstrated that the production of hydrogen from an optimized mixture of Mg + 5wt%Ni + 5 wt.% C is robust enough to be implemented on a E-bike. This fully demonstrated that the production of hydrogen from hydrolysis should be considered as an alternative as it avoids also its storage.

The life cycle analysis highlights that the Ni present in the powder mixture has a very huge impact especially on the human health and the resources. It is pointed out that if the impact of Ni is suppressed or at least drastically reduced, the hydrolysis process is far better than the steam reforming from methane process which is used to produce 95% of the hydrogen in the world.

Therefore, the (bulk) composites were used for the generation of hydrogen and a complete reaction was reported for the composite containing 90wt.% Mg in total within 20 minutes. This allows (i) suppressing the energetic ball milling usually used and (ii) reducing the amount of Ni by a factor of 2 and so minimizing the impact of it on both the human health and the resources.

Finally, this demonstrates that coupling fundamental research (the search of new ternary compound in the Mg rich part of the Nd-Ni-Mg Gibbs triangle) and very applied ones (production of hydrogen by hydrolysis with the development of a prototype) is possible.

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