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Hydrogen generation from magnesium alloys: offering a second life to waste and preparing the industrialization of the process

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ABSTRACT
Hydrogen can be produced by hydrolysis of non recycle Mg alloys. It appears as a good solution for clean energy production. Nevertheless, before thinking about an industrialization of the process, several points should be clarified. We demontrsate here thatthe role of zinc is not as negligible as often status because of the formation of the solid solution $Mg_{0.97}Zn_{0.03}$ that is not favourable for hydrolysis. The presence in the alloy of the intermetallic Mg17Al12 is beneficial because of the establishment of a galvanic coupling.Also, using very fine chips is not favourable for hydrolysis because of the formation of an oxide layer on the surface. Using larger chips (0.6 mm thick) is better from hydrolysis point of view but also looking at the cost of machining the bulk alloys. Several mill apparatus are tested and it is shown that the milling mode is not the driving force but only the total input energy is. Milling at low temperature is not beneficial as the ductile to brittle transition is not reached under liquid nitrogen. A minimum of 5wt% of nickel must be added to the alloys to get the best hydrolysis properties. Finally, the ball milling can be done under nitrogen in replacement of expensive argon but also under air (with a very little decrease of the hydrolysis performances) if the milling is performed in close vial.
This gives us the principal trends for the industrialization of the process.

KEYWORDS:* *Hydrogen production, hydrolysis, magnesium alloys, milling, industrialization.

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I. INTRODUCTION

From the last decades, hydrogen is claimed to be the energy of the future for the more optimistic person and a clean energy carrier for the most pessimistic one [1, 2]. Although there might be a mass production of hydrogen using renewable energy in the long term, fossil fuels are the major source for its production today [3, 4]. The hydrogen production sources were about 48% from natural gas, 30% from fossil oil and 18 %from coal and the rest with electricity via water electrolysis [4].

It is well known that it has higher energy content per unit of mass than oil and natural gas. It is readily available in large amounts in water and does not produce harmful emission. Nevertheless, the storage of hydrogen is still not completely solved. Hydrogen can either be store in the form of molecular hydrogen in pressurized vessels [5], liquefied hydrogen tanks [6] and carbon materials [7]. Storage in the form of atomic hydrogen in metal hydrides [8] or in the form of hydride ion in protide compounds such as alanates [9] and borohydrides [10] offer other alternatives. Nevertheless, whatever the way of storage chosen, some cost, security, weight or volume capacity drawbacks often appear. Moreover, hydrogen production always appears as one of the main challenge. If actually, 95% of hydrogen is produce by reforming of fossil fuel [11], efforts have been devoted to electrolysis and dark fermentation [12, 13].Some authors state the global hydrogen production amount of about 500 billion Nm3/yr [14]. Also,thermolysis (usually followed by hydrolysis of the by product) of NH_3BH_3 or equivalent compounds [15] has been studied as well as hydrolysis of borohydrides (MBH_4 and especially $NaBH_4$). In this last case, the byproduct $NaBO_2$ can be considered as relatively toxic. In fact the lethal dose 50 (LD50 = 2.33 mg/Kg) is ranked 2 on the Hodge and Sterner scale (which count 6 level from extremely toxic (1) to relatively inoffensive (6)).

Hydrogen production based on hydrolysis reaction of various materials has been recognized. This method is promising because as no additional energy is required (low temperature operation) and it offers the possibility to produce delocalized and rather pure hydrogen. Many kind of materials such as complex hydrides [16],

Metal and/or intermetallics [17, 18]and metal hydride [19] have been tried in the literature. Among these materials, magnesium metal has attracted much attention for hydrogen production via hydrolysis reaction due to its electrochemical activity, low density, low cost, abundant and non toxic product. Magnesium and magnesium hydride react with water according to the following equations (Eq. 1 and 2 respectively):

$$Mg + 2H_2O = Mg(OH)_2 + H_2 \qquad \text{(Eq.1)}$$

$$MgH_2 + 2H_2O = Mg(OH)_2 + 2H_2 \qquad \text{(Eq.2)}$$

The theoretical hydrogen yield is 8.2 wt.% and 15.2 wt.% (no water included in the calculation) for Mg and its hydride respectively. The Mg hydrolysis reaction is always blocked by the formation of a passive hydroxide layer $Mg(OH)_2$ and cannot be carried out completely. In order to improve the hydrolysis performance of Mg powder, different solutions have been investigated.

It has been demonstrated that hydrogen generation is improved via the interaction of magnesium with organic acids or via applying ultrasonic irradiation (more especially in the case of MgH_2)[20] or also using ball milling with additives [21, 22].

In previous works [22, 23] the positive role of carbon additives on $MgH_2$and/or Mg hydrolysis reactionwas demonstrated. Also, the synergetic effect of graphite and transition metals, like Ni, was also investigated. Additionally, two metal oxides (Nb_2O_5 and V_2O_5) were co-milled with Mg and the hydrolysis reaction was studied. After that, the activation energies of best mixtures were calculated using Avrami-Erofeev model. Finally, the feasibility of the onboard hydrogen production, from the hydrolysis of MgH_2, to supply PEMFC has also been investigated [24].

Hydrolysis with magnesium appears as a good solution from an environmental point of view but the cost could be rather high (e.g. considering the price of magnesium at 2$/Kg, that lead to almost 25$ per kg of H_2). Therefore, to reduce the cost, using magnesium alloys residue is of major interest [25-26]. In the present paper, we study the hydrolysis of ball milled magnesium alloys scraps and the influence of (i) ball milling condition and atmosphere (to be as closed as possible to an industrial route) and (ii) nature of the initial chips size. The role of the compounds present in the alloys is also highlighted.

II. EXPERIMENTAL PART

AZ91 Mg alloy was supplied by an aeronautical company in form of large pieces (10*20*50 cm) that were machined to get chips from it. Mg powder (Stream Chemicals, 99.9%) was used as starting materials. Graphite powder G (99%, Aldrich), Ni and Zn powders (Alpha, 99.9%) were used as additive.

Mg alloy (or mixtures of powders) milling was performed under various atmosphere (AR, H2, N2 and Air) at room temperature in various miller (planetary ball mill (Fritsch P5), cryogenic 2D vibratory (RetshCryomill), 3D vibratory(Spex 8000)). Stainless steel balls (10 mm diameter) and vials were used. The ball-to-powder mass ratio was fixed to 17:1 in all cases. The milling at 250 rpm (P5), 4Hz (Cryo mill and 3D mill) with the sequence of 15 minutes of milling followed by 2 minutes of rest. When milling under N_2, Ar and H_2, the pressure was fixed at 5 bars and the vial was recharged every 30 minutes to ensure a constant pressure.

To minimize the air exposure, the materials were stored in argon-filled glove box. Nevertheless, before any hydrolysis tests, it was mandatory to expose the sample to air but we succeed to limit it to a maximum of 5 minutes.

Hydrolysis tests (Room temperature and atmospheric pressure, 20 mg of sample with 100ml of salted water) were performed following the same procedure described in references [22, 27].

The samples were characterized by X-ray diffraction (XRD) using a Philips PANalyticalX'Pert (PW1820) diffractometer with Cu $K_{\alpha 1}$ radiation, laser granulometry in ethanol (Malvern Mastersizer hydro 2000® analyzer) and scanning electron microscopy (TESCAN VEGA3 SB microscope coupled to an EDS detector). The crystalline phases identification was done using the ICDD.

III. RESULTS AND DISCUSSION

As our goal was to use AZ91 alloy, the first step was to compare a mixture of ball milled Mg + 9wt%Al+1wt.%Zn (named ALZN) with some AZ91 powders. The X-ray diffraction pattern is presented in figure 1.

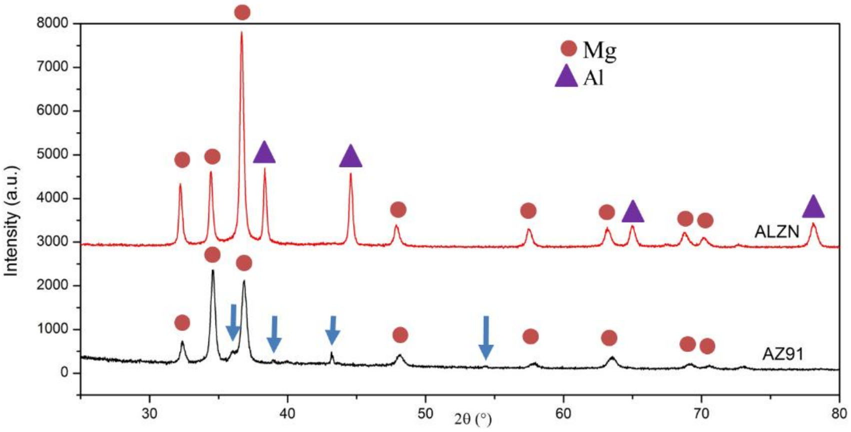

Figure 1 : *X-ray diffraction pattern of [Mg + 9wt%Al+1wt.%Zn (named ALZN)] and AZ91 alloy.*

As expected, on the mixture of Mg-Al-Zn, the only detected peaks are related to magnesium and aluminium. No alloying accurs during ball milling as the duration was rather limited (3 hours here). As the weight percentage of zinc is only 1wt.%, it cannot be detected. The diffractogramm of the alloy is slightly different. First, no peak related to aluminium can be seen. That means that Al reacted with magnesium. It is known that when the Al content is higher than 3wt.%, the formation of the intermetallic $Mg_{17}Al_{12}$ can be observed. The extra peaks marked with arrows on figure 1 can be indexed with $Mg_{17}Al_{12}$. Second, the second peak related to magnesium (e.g. the (002)) presents a higher intensity than expected highlighting a preferred orientation along the (00l) direction. Finally, the magnesium peaks are broader and asymmetric. A deconvolution of the peaks revealed that each peak is composed of 2distinguished signals. This is due to the existence of a solid solution of Zn into magnesium with a composition $Mg_{0.97}Zn_{0.03}$ [28]. From the XRD data it was possible to get the cell parameter of the solid solution (i.e. a = 3.189 and c = 5.179A) in good agreement with ICSD data base. The volume of the solid solution is 45.6A^3 as the one of the magnesium cell is 46.3 A^3.

The presence of Zn as solid solution into magnesium can have an influence on the hydrolysis. The hydrolysis of magnesium is limited by the formation of the non solubleMg(OH)2 phase. As $Zn(OH)_2$ phase is even less soluble (*e.g.* $K_S(Mg(OH)_2) = 10^{-11}$ $mol^3.L^{-3}$ and $K_S(Zn(OH)_2) = 3 * 10^{-16}$ $mol^3.L^{-3}$), the presence of metallic Zn would hinder the reaction between water and metal. For the same reason, the solubility of the solid solution is expected to be lower than the one of $Mg(OH)_2$ (*e.g.* expected to be in between the one of $Mg(OH)_2$ and $Zn (OH)_2$).

Table 1 : Median diameter (measured from granulometry) of the various powders used.

Sample	Initial Mg	Mg+Ni+C BM 3h	Mg+Al+Zn BM 3h	Mg+Al+Zn+**C** BM 3h	AZ91 BM 3h	AZ91+C BM 3h
d_{50} (mm)	230	59	78	59	51	39

Another important parameter for hydrolysis is the surface in contact with water during the reaction. As ball milling was performed for rather short time and magnesium is ductile, it is possible to estimate that the specific surface is directly proportional to the particles size. Therefore, the mean diameter of all the powders used are reported in table 1. The first two columns are references materials (*i.e.* initial Mg and the optimized patented powder Mg +5wt.%Ni + 5 wt.%C). Comparing the median diameter for (Mg+Al+Zn) ball milled for 3 hours without and with C, it is obvious that the presence of graphite allow a decrease of the particle size as already reported [23, 25, 27]. Comparing AZ91 and its equivalent powder composition (*i.e.* Mg +9wt%Al+1wt.%Zn) highlights that as AZ91 is more brittle than magnesium (e.g. the hardness are 63 HB and 45 HB, the tensile strength are 230MPa and 170 MPA, the elongation are 3% and 6.1% for AZ91 and Mg respectively) the particles are smaller for AZ91 (*e.g.* 78 to 51 mm). As previously mentioned, the addition of C allow to decrease a little more the size (from 51 to 39).

On figure 2, we present the hydrolysis performances of the various mixtures. It highlights that the AZ91 alloy milled for the same duration than a mixture of Mg+Al+Zn (with the same composition) shows better kinetic. For example, after 10 minutes, the yield is 60% for the alloy for only 30% for the powder mixture. Also, as shown by others [22, 23, 27], the addition of carbon leads to an increase of the kinetic.

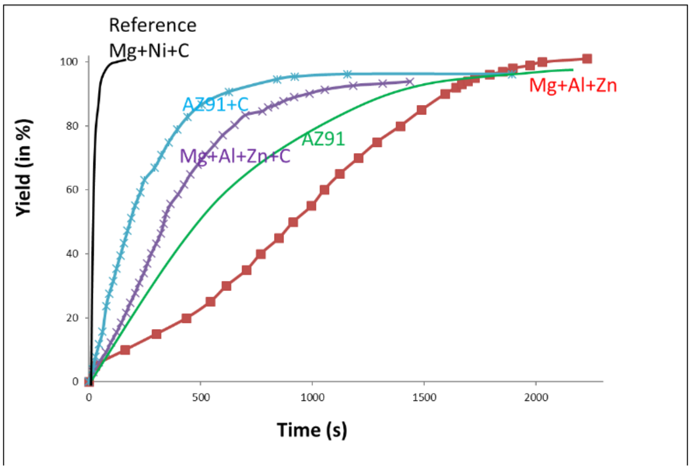

Figure 2 : *Hydrolysis yield for MgAlZn, MgAlZn + C, AZ91 and AZ91 + C*

The different behaviour is linked with both the granulometry and the chemical composition. AZ91alloy and the powder mixture do not have the same mechanical properties (AZ91 is more brittle) and so, as seen on table 1, the ball milling will allow obtaining smaller particle (so higher specific surface). In addition, in the AZ91 alloy, an intermetallic $Mg_{17}Al_{12}$ exist and a galvanic coupling [22] will exist between $Mg_{17}Al_{12}$ and the magnesium. Therefore, the corrosion (i.e. the hydrogen production) will be enhanced. As previously mentioned, the presence of Zn in the AZ91 alloy leads to the formation of a solid solution $Mg_{0.97}Zn_{0.03}$. This solid solution will not favour the hydrolysis because of the solubility of Zn(OH)2 compared with the one of Mg(OH)2. Nevertheless, the influence of this solid solution will be rather limited because : (i) the amount of solid solution is very low (as the amount of Zn in the alloy is about 1wt.%) and (ii) the solubility of $MgCl_2$ and $ZnCl_2$ are both high and not so different (*e.g.* 542 and 376 g/L respectively).

Nevertheless, it should be pointed out that the hydrolysis performances are still far from the one of the optimized Mg+Ni+C powder (as seen in figure 2).

In order to further investigate the role of the solid solution $Mg_{0.97}Zn_{0.03}$, we synthesized it in a sealed tantalum tube. The XRD pattern reveals only the presence of the solid solution with cell parameter a = 3.189A and c = 5.179A in agreement with the JCPDS card.

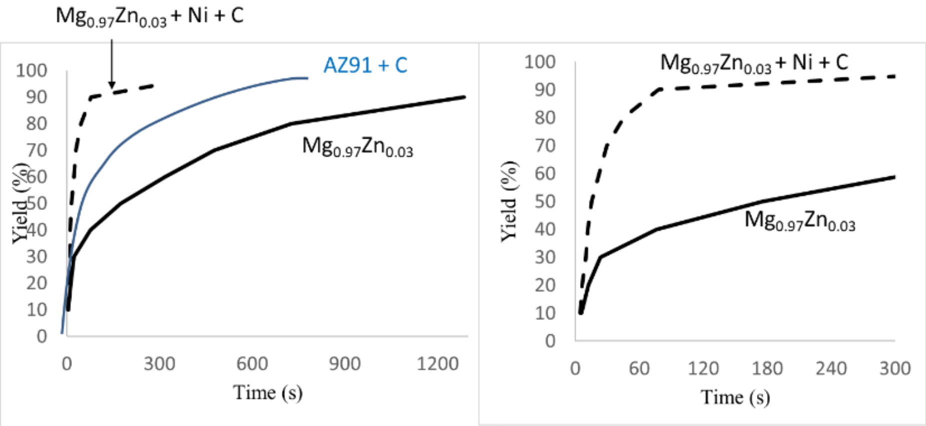

Figure 3 : *Hydrogen production by hydrolysis with the solid solution $Mg_{0.97}Zn_{0.03}$ without additives and with Ni and C (AZ91 BM with C is also shown in order to compare). On the left, the full range of the reaction and on the right, only the first 5 minutes.*

The hydrolysis performances of the solid solution were measured and it is presented in figure3. With comparable granulometry (the mechanical behaviour of the solid solution is very close to the one of pure magnesium), the behaviour of pure magnesium is slightly better but the difference is very weak. For example, comparing the Mg+Ni+C with the mixture solid solution+Ni+C, the yield is respectively 96 and 88 after 60 secondes (and 62 versus 55% after 20 secondes). The very similar behaviour between the solid solution and the pure magnesium is related to the very similar mechanical and electrochemical properties. Therefore, the presence of $Mg_{0.97}Zn_{0.03}$ as almost no incidence on the hydrolysis performances.

Often, researchers are looking for fine and homogeneous powders. Nevertheless, the idea of hydrolysis is usually to offer a second life to “trashed” magnesium alloy. Therefore, these alloys will be bulk alloy and a simple way to avoid the use of bulk is to produce chips from it. Then, we produced 2 kind of chips : large ones (0.6 mm thick) and fine ones (0.02 mm thick). The chips were ball milled for 3 hours with carbon and sieved. The result of sieving is presented in table 2.

Table 2 : Relative weight amount (± 2%) of each class of granulometry ranging from higher than 200 mm to lower than 50 mm for the larger chips (0.6 mm) and the finer ones (0.02mm).

	Particles size			
	>200 µm	[200 , 100] µm	[100, 50] µm	< 50 µm
Chips of 0.02 mm	24	14	17	45
Chips of 0.6 mm	19	9	17	55

From this table, it is interesting to notice that the finer chips lead to the formation of lesser fines particles. At a first glance, such result is surprising but in fact, the form factor have to be considered. The difference between the two kinds of chips is only the thickness as the other dimensions are more or less the same. Therefore, a decrease in thickness lead to an increase of the form factor and then to a decrease of the ball milling efficiency. Considering a potential application for hydrogen storage, such result is encouraging because that means that fine chips are not required (meaning less machining and less oxidation of the product during storage).

The hydrolysis behaviour of the powder resulting from ball milling for 0.5, 1 and 3 hours of both types of chips is presented on figure 4.

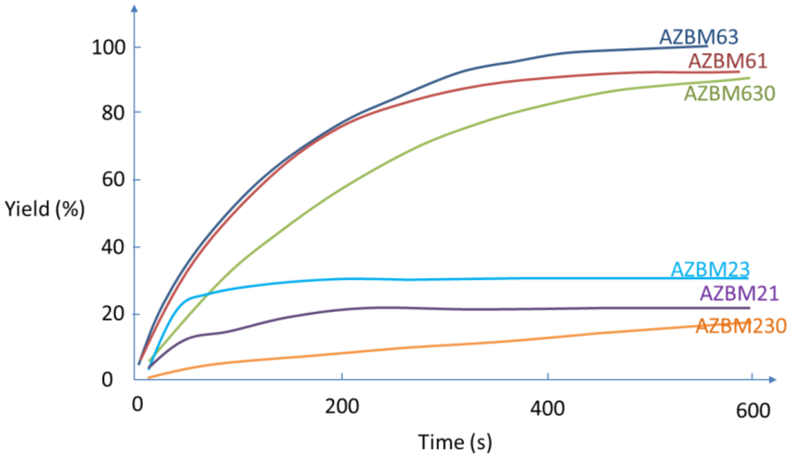

Figure4: *Hydrogen production by hydrolysis with AZ91 +C BM for different time with 2 initial chips size (for example AZBM61 referred to AZ91 0.6 mm chips sizes and ball milled for 1hour)*

For all samples, increasing the milling time from 0.5 (30 minutes) to 3 hours lead to a slight improvement of the kinetic. This can be correlated with the decrease of the particles size which increase the reaction surface. If the larger chips give rather good kinetic and almost full capacity (yield of 100%), the finer ones show a saturation around 30% after only 1 minute. Considering the previous physico-chemical properties presented, such phenomenon is unexpected. In fact, to explain it, we have to look closely at the chemical composition. When the chips are too thick, the surface oxidation of magnesium can become predominant and then, no hydrolysis reaction can take place. As a matter of fact, considering chips of 5mm*2mm*thickness (*i.e.* 0.6 or 0.02 mm), if the thickness of magnesium oxide is only 5 µm, that gives 50% of oxides for the 0.02 mm chips and less than 2% for the larger ones. To verify our hypothesis, we add some chloridric acid (HCl, 2 mol/L) when saturation starts (*i.e.*at 30% yield). Such addition permit to dissolve the MgO layer and the yield increase up to 45% and saturate again. It highlights that the MgO layer represent more or less half of the total material for finer chips. As previously mentioned, this is promising for application as no fine chips would be required (and even have to be avoided).

Still considering a potential application and then an industrialization of the process, the possible scale up should be examined. For that purpose, different milling tools has been tested. Often time, cryo milling is mentioned when considering milling of ductile powders (under liquid nitrogen, some ductile metals can became brittle). Therefore, we applied cryomilling on the chips (*e.g.* 0.6 and 0.02 mm thick).

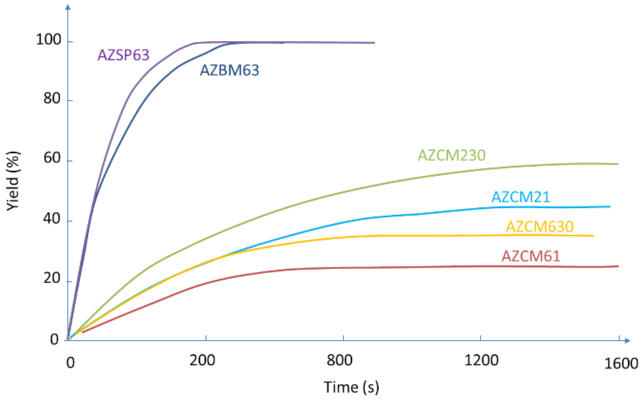

Figure 5: *Hydrogen production by hydrolysis with AZ91 +C milled with different milling apparatus and different time (with 0.6 and 0,02 mm chips sizes). CM refereed to cryomill, BM to ball mill, and SP to 3D vibratory mill.*

The results are summarized on figure 5. It is clear from this figure that the hydrolysis of powders produced by cryomilling give very poor results (both kinetics and total yield). In fact, the liquid nitrogen temperature is not low enough to induce the transition from ductile to brittle for magnesium. Therefore, the magnesium is still ductile and as the energy of milling is rather low, the efficiency of milling is the lowest one and then the hydrolysis performances are weak too. After cryomilled for 0.5 or 1 hour, the SEM observations (not presented here) highlight that we got essentially chips and not a lot of powder (less than 5 to 10%). This demonstrates the low efficiency of milling. By cryomilling, whatever the chips thickness, the performances are rather similar. Nevertheless, the smallest particles give the best results (which is in contradiction with the previous observation). Once again the oxide present on the surface is probably the explanation : the smallest thickness had the larger oxide content (relatively); this latest one will be easily milled at low temperature ; this brittle particles will then increase the efficiency of milling and then the hydrolysis performances.

It also appears from figure 5 that the efficient milling are the planetary and the vibratory one. In fact, the energy of both milling are rather similar so that we can conclude that the important point is the total energy input and not the type of milling and/or the milling duration [29]. From an industrial point of view, the scale up with planetary milling is rather common as the one with vibratory is probably more complex. Therefore, the scale up will be possible by considering a total energy input similar to the one used here.

The life cycle analysis presented in [30] has shown that nickel is not favourable considering especially human health and resources. Then, it is important to try to suppress nickel (or to replace it by a more favourable element). Considering also that more than half of the magnesium alloys are not recycle because of financial consideration (the cost of recycling is too high for the low grade magnesium alloys), it is important to study if the replacement of pure magnesium by magnesium alloy can allow to supress or at least to reduce the amount of nickel in the powder. For that purpose, mixture containing 0, 2 and 5 wt.% nickel has been prepared and tested. The hydrolysis performances are presented on figure 6.

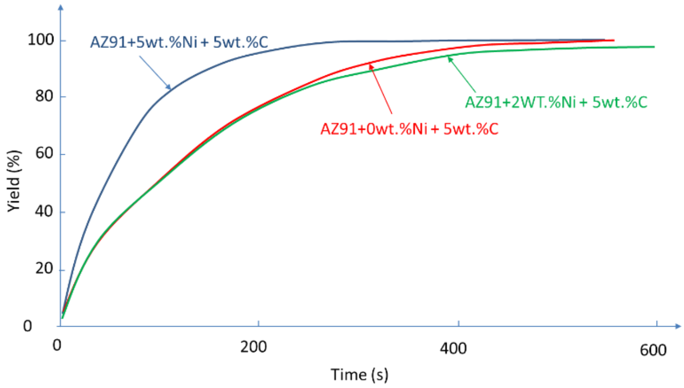

Figure 6 : *Hydrogen production by hydrolysis with AZ91 + 5wt.%C + 0, 2 and 5 wt.% Ni ball milled (planetary mill) for 3hours (with 0.6 mm chips sizes)*

The first important thing is that whatever the content of nickel, a total reaction can be achieved. Nevertheless, the full capacity (100% yield) is obtained after almost 10 minutes when 0 or 2 wt.% of nickel whereas, only 5 minutes are required when 5wt% are added. As previously mentioned [21, 22, 27], the presence of nickel lead to a galvanic coupling with magnesium and then increase the corrosion (*i.e.* the H_2 production). If the quantity of nickel is too low, the galvanic coupling is very weak and then the contribution of it to the corrosion behavior is negligible. Also, using magnesium alloy in replacement of pure magnesium do not improve the kinetic (it even slightly slow it) but as it reduce the cost and the environmental impact, it is suitable.

One of the last point to be considered for an industrialization of the process is the milling atmosphere. For lab experiment, argon is the most used gas. In order to increase the hydrogen production (but reducing the performance as seen in [31]) ball milling can also be done under hydrogen. Nevertheless, in industry, the hydrogen will be probably too complicated (because of hazardous properties), argon will be too expensive and replaced by nitrogen (also considered as inert gas but cheaper) and more often air will be used. For that purpose, we compared the results of hydrolysis for powders obtained with the 4 different atmosphere of milling and presented the results on figure7.

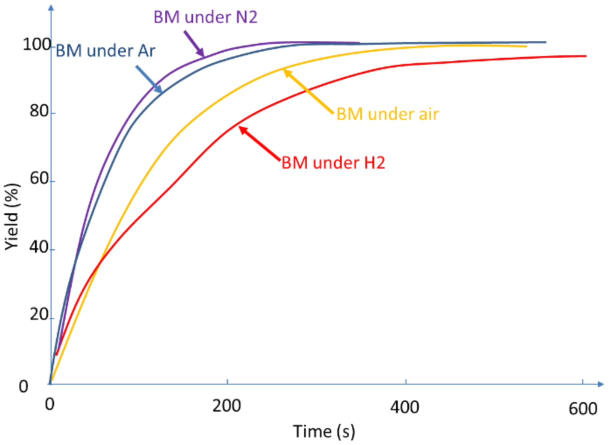

Figure 7: *Hydrogen production by hydrolysis with AZ91 + 5wt.%C + 5 wt.% Ni ball milled (planetary mill) for 3hours (with 0.6 mm chips sizes) under 4 different atmosphere (i.e. Ar, Air,* N_2 *and* H_2*).*

The first interesting point is the behaviour of the powder ball milled under H2. As expected from previous results, a decrease of the reaction rate is observed and it is attributed to the fact that the MgH_2 formed during milling is less reactive [21, 31] than magnesium. 80% yield is obtained after 5 minutes whereas the full capacity is reached when ball milling is performed under Ar. It is worth pointing out that as the powder contains a little less than 5% of magnesium hydride, the full capacity of 100% correspond to an increase of the total H_2 production of almost 5%.

It is also interesting to notice that the kinetic is not as affected as when pure magnesium was used. This is directly linked with the fact that milling pure magnesium under hydrogen leads to the formation of more MgH_2 than when magnesium alloy is used.

The second interesting point is that the powders ball milled under argon or nitrogen give almost the same results. The difference cannot be considered as significant and can even be attributed to the purity of each gas. In the case of magnesium or magnesium alloy, nitrogen is often considered as an inert gas as the formation of nitrides do not occur under standard conditions.

The third point is theresults obtained for the powder ball milled under air. From figure 7, it is clear that the hydrolysis properties are not so affected by the milling under air which is very promising for industrial application (allowing a reduction of the cost). Nevertheless, such result is not that surprising if we considered that the milling is performed under closed conditions. In our case, we use vial of 100 mL and 4g of magnesium alloy which give us a ratio O_2/Mg of about 0.5mol%. We even must status that our results are worse than expected and it can be explained by the non-respect of the closed condition (the jar may present some leaks during milling). Once again, such result is very promising for industrial application (*i.e.*milling under air is possible and the jar do not need to be perfectly tight).

IV. CONCLUSION

We demonstrate that trashed AZ91 alloys can be recycled to produce hydrogen by hydrolysis. The role of zinc was seen to be not as negligible as often status because of the formation of the solid solution $Mg_{0.97}Zn_{0.03}$ that is not favourable for hydrolysis. The presence in the alloy of Mg17Al12 is beneficial because of the establishment of a galvanic coupling between the intermetallic and the magnesium.

The use of very fine chips is not favourable for hydrolysis because of the formation of the oxide layer on the surface. We demonstrate that using larger chips (0.6 mm thick) is better.

For the scale up, the only point to be considered is the total milling energy input and not the mode of milling. Also milling at low temperature was seen to not be beneficial as the ductile to brittle transition is not reached under liquid nitrogen. For industrial perspective, planetary milling can be considered.

We also demonstrate that a minimum of 5wt.% of nickel is necessary to get rather good hydrolysis properties. As it is known to be not fair for human health and resources, that leaves us with the following choice : having optimal hydrolysis performances (but being unfair for environment because of nickel) or operating a system with lower kinetic.

Finally, for industrialization, cheap nitrogen gas can be used as inert gas but operating in a close system could allow to perform milling under air with a very little loose of hydrolysis performances.

All this results give us a green light for green hydrogen production from trashed magnesium alloy offering them a second life.

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