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Effect of ball milling in presence of additives (Graphite, AlCl₃, MgCl₂ and NaCl) on the hydrolysis performances of Mg₁₇Al₁₂

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Abstract

In most of the Mg-Al alloys, Al forms with Mg the intermetallic compound Mg₁₇Al₁₂. In order to understand the hydrogen production from the Mg-Al alloys waste by the hydrolysis reaction in “model” seawater (*i.e.* 3.5 wt. % NaCl), hydrolysis with Mg₁₇Al₁₂ was investigated. The effect of ball milling time, the nature of the additives (graphite, NaCl, MgCl₂ and AlCl₃) and the synergetic effects of both graphite and AlCl₃ were investigated. It has been established that increasing ball milling time up to 5h is necessary to activate the intermetallic and to decrease sufficiently its crystallites and particles size. On one hand, the presence of AlCl₃ provides the best hydrolysis performance (14 % of the theoretical hydrogen volume in 1h). On the other hand, the mixture obtained by simultaneous addition of graphite and AlCl₃ shows the best hydrolysis performances with 16% of the theoretical H₂ volume reached in 1h.

Keywords: Mg₁₇Al₁₂; hydrogen production; ball milling; hydrolysis; Mg-Al alloys.

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1. Introduction

Magnesium alloys are used as structural materials in various industries where the intended application requires weight reduction (aeronautics, automotive, ...) [1-3]. However, the problem that limits the extension of the use of Mg-based alloys is related to their corrosion. In recent years, many commercial Mg alloys (with Al, Zn, RE,...) have been developed [4].

Nowadays, only magnesium-based alloy wastes class 1 and 2 (*i.e.* high purity) are recycled to secondary ingots [5, 6]. It has been shown that other magnesium-based alloy wastes can be used to generate H₂ by the hydrolysis reaction [7-13]. Hydrolysis with magnesium-based materials is an electrochemical reaction where Mg is oxidized to Mg²⁺ (*i.e.* Mg corrosion) and water is reduced to produce H₂ gas [9].

AZ91 is one of the most used magnesium alloys. Our objective is to produce hydrogen by the hydrolysis reaction with AZ91 alloy waste in a solution similar to seawater (*i.e.* 3.5 wt.% of NaCl) without the use of external catalyst. Previously, Uan *et al.* reported that AZ91 can generate H₂ by hydrolysis and the reaction performance was improved using a Pt/Ti catalyst due to the galvanic coupling between Mg and Pt [7].

The as-cast AZ91 microstructure has typically a primary α -phase matrix (Mg matrix) and a β -phase precipitate (Mg₁₇Al₁₂ intermetallic phase). As a galvanic coupling exists between the β -phase and the magnesium, depending on the amount and the specific surface of the β -phase (and so the surface contact between both phases), two opposite behavior can be observed: acceleration of the corrosion rate or either creation of a corrosion barrier hindering corrosion [14-17].

In order to better understand and then to enhance the hydrolysis performance of AZ alloys, the behavior of the two main components (*i.e.* Mg and Mg₁₇Al₁₂) has to be studied separately. The hydrolysis of Mg have been widely reported [18-28] whereas the "Mg₁₇Al₁₂ – H₂" subject is not sufficiently investigated. Previous studies have shown that Mg₁₇Al₁₂ can be used for hydrogen storage [29-32] while the production of hydrogen by the hydrolysis reaction has never been reported.

Magnesium hydrolysis can be improved by ball milling with additives. Considering the similarity between Mg and $Mg_{17}Al_{12}$, the effect of ball milling on the hydrolysis performance (*i.e.* yield and kinetics) of $Mg_{17}Al_{12}$ using relatively cheap additives such as graphite, NaCl, $MgCl_2$ and $AlCl_3$ is relevant. Graphite improved the hydrolysis performance of Mg and WE43 due to the formation of a thin layer which limits the oxidation and prevents the adhesion of $Mg(OH)_2$ to Mg surface [23]. Ball milling with 3 mol.% of NaCl was optimum to improve the hydrolysis performance of MgH_2 where NaCl facilitates the reduction of the particles size and the creation of surface defects [33]. Total hydrolysis reaction (*i.e.* yield = 100%) was reported for Mg in the ball milled mixture Mg with 10 mol. % of $MgCl_2$ [27]. The enhancement was attributed to the extra heat generated by the exothermic dissolution of $MgCl_2$. Similarly, the exothermic dissolution of $AlCl_3$ increases the temperature and generates HCl in the reaction medium which dissolve the formed $Mg(OH)_2$ and improve the hydrolysis reaction [26].

The effects of ball milling time, heteromaterials (Graphite, NaCl, $MgCl_2$ and $AlCl_3$) addition during the mechanical process and the synergetic effect of both graphite and $AlCl_3$ were also studied. To our knowledge, no previous work has investigated the hydrolysis of $Mg_{17}Al_{12}$; in order to better understand the hydrolysis of AZ magnesium alloy. Experimental results show that ball milling increases the hydrolysis performance of the intermetallic in a 3.5 wt.% NaCl solution (*i.e.* similar to seawater) especially when milled in presence of graphite and $AlCl_3$ (e.g. simultaneous addition) leading to the best result with a hydrogen production of $136 \text{ mL} \cdot (\text{g of powder})^{-1}$ which corresponds to a yield of 16%. The results are explained in terms of microstructural (XRD and SEM-EDS analysis) and morphological (SEM-Granulometry) effects.

2. Experimental Procedure

2.1. $Mg_{17}Al_{12}$ synthesis

Based on the binary phase diagram of Mg and Al, commercial magnesium and aluminum powders were mixed with 17:12 atomic ratio by an ultrasonic homogenizer. This homogeneous mixture was put into stainless-steel container and closed in a glovebox to get fully rid of air contamination.

Afterwards, the container was heated with a heating rate of 2 K/min up to 813K (higher than the congruent melting temperature of $\text{Mg}_{17}\text{Al}_{12}$ because the appearance of the liquid phase is beneficial for the diffusion process, which is the key for the alloying of $\text{Mg}_{17}\text{Al}_{12}$), and kept at this temperature for 2h. Then the temperature was decreased to 723K (melting temperature of $\text{Mg}_{17}\text{Al}_{12}$) with a rate of 4.5 K/h. Finally, cooling down to room temperature was done by turning off the furnace.

2.2. Ball milling

Graphite (G) (Fisher Scientific), sodium chloride NaCl (Fisher Scientific, 99.5%), anhydrous magnesium chloride MgCl_2 (Aldrich, 98%) and anhydrous aluminum chloride AlCl_3 (Acros organics, 98.5%) powders were used as milling additives. The chlorides were stored in a glove box to avoid hydration. Based on our previous studies [13, 23], we have adopted the addition of 5 wt. % of additives (*i.e.* G, NaCl, MgCl_2 or AlCl_3) during ball milling. The $\text{Mg}_{17}\text{Al}_{12}$ - X (X = G, NaCl, MgCl_2 or AlCl_3) mixtures were prepared by ball milling (using a Fritsch Pulverisette ® 5) in a stainless-steel vial under argon with the sequence: 15 min of continuous milling followed by 2 min of rest (to allow the system to cool down). The ball to powder weight ratio was 17:1 corresponding to 1.18 g of powder and 5 stainless steel balls (10 mm of diameter) and the rotation speed was fixed to 250 rpm. The milling vial was handled in a glove box filled with purified argon.

2.3. Characterization

The hydrolysis reaction was carried out in a salted water solution (3.5 wt % NaCl) at room temperature (more details can be found in reference [34]). Hydrogen production is presented as the conversion yield (%), which is defined as the volume of produced hydrogen over the theoretical volume of hydrogen if $\text{Mg}_{17}\text{Al}_{12}$ powder is completely consumed.

The samples were characterized by X-ray diffraction (XRD) using a Philips PANalyticalX'Pert (PW1820) diffractometer with Cu $\text{K}\alpha_1$ radiation ($\lambda=1.5405\text{\AA}$). Crystallites sizes were estimated

from XRD refinement using EVA software (according to the weighted Scherrer formula) and the cell parameters were evaluated from Rietveld Refinement using FullProf software. Scanning Electron Microscopy (SEM) coupled with Energy Dispersive Spectrometer (EDS) observations were made using a TESCAN VEGA3 SB microscope. Particles size distribution was evaluated by laser granulometry using a MASTERSIZER2000 from Malvern®.

3. Results and discussion

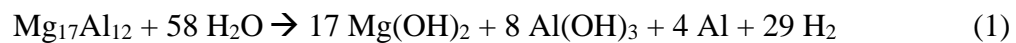
3.1. Hydrolysis reaction

Pure Mg₁₇Al₁₂ was synthesized as shown from X-ray diffraction pattern [35]. The hydrolysis reaction of Mg₁₇Al₁₂ was performed in 0.6M HCl until the complete dissolution of the intermetallic is achieved to evaluate the maximum generation of H₂.

The X-ray diffractogram of the solid product obtained after neutralization with KOH and drying (Supplementary material figure 1) revealed the presence of Mg(OH)₂, MgCl₂.6H₂O and Al(OH)₃ and the absence of peaks related to Mg₁₇Al₁₂ justifying the total reaction. Mg₁₇Al₁₂ generates 85% of the theoretical H₂ volume considering that both Mg and Al react (Supplementary material figure 2). During the hydrolysis reaction, OH⁻ ions are generated in the solution increasing the medium's pH. According to Pourbaix diagram of magnesium at the Open Current Potential of Mg₁₇Al₁₂ (E= -1.2 V/ECS), the corrosion zone extends to pH = 8.5 while for aluminum, the passivation zone extends from pH=1.5 [36].

Through the hydrolysis reaction, Mg(OH)₂ and Al(OH)₃ protective films are formed preventing the diffusion of water to the unreacted Mg and Al atoms. Since Mg is more reactive than Al and Al(OH)₃ is more protective than Mg(OH)₂, we consider that all Mg atoms and 2/3 of Al atoms are oxidized (*i.e.* the number of reactive aluminum atoms is calculated based on the hydrolysis yield results).

Then, the equation for the hydrolysis reaction with Mg₁₇Al₁₂ can be written as:



The use of acids increases the corrosive effect but for practical application, handling with relatively neutral solutions such as seawater (*i.e.* aqueous NaCl solution) is preferable.

3.2. Ball milling time

The As-Cast $Mg_{17}Al_{12}$ barely reacts in 3.5 wt.% aqueous NaCl solution.

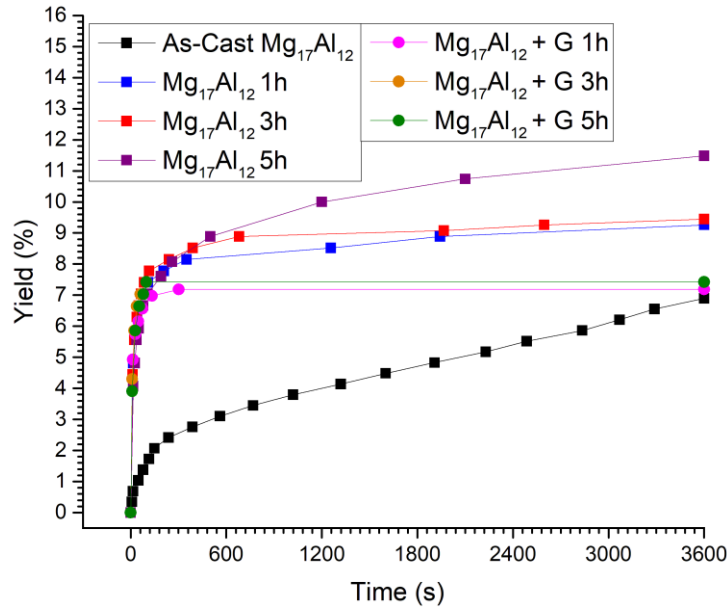


Figure 1: Hydrogen generation by: as-cast $Mg_{17}Al_{12}$, $Mg_{17}Al_{12}$ ball milled for 1h, 3h and 5h, and $Mg_{17}Al_{12}$ ball milled with graphite (denoted $Mg_{17}Al_{12} + G$) for 1h, 3h and 5h.

Only 6% of the theoretical hydrogen volume are generated after 1 hour of reaction (figure 1). Ball milling of magnesium under inert atmosphere (*i.e.* Argon atmosphere) was proved beneficial to increase the hydrolysis reactivity of the materials. The effect of ball milling duration on the reactivity of $Mg_{17}Al_{12}$ was studied by varying the milling time (*e.g.* 1h, 3h and 5h).

$Mg_{17}Al_{12}$ has a cubic unit cell. The cell parameter of the synthesized $Mg_{17}Al_{12}$ is 10.53 Å and stay approximately constant after ball milling (maximum variation of 0.15%, *cf* figure 3).

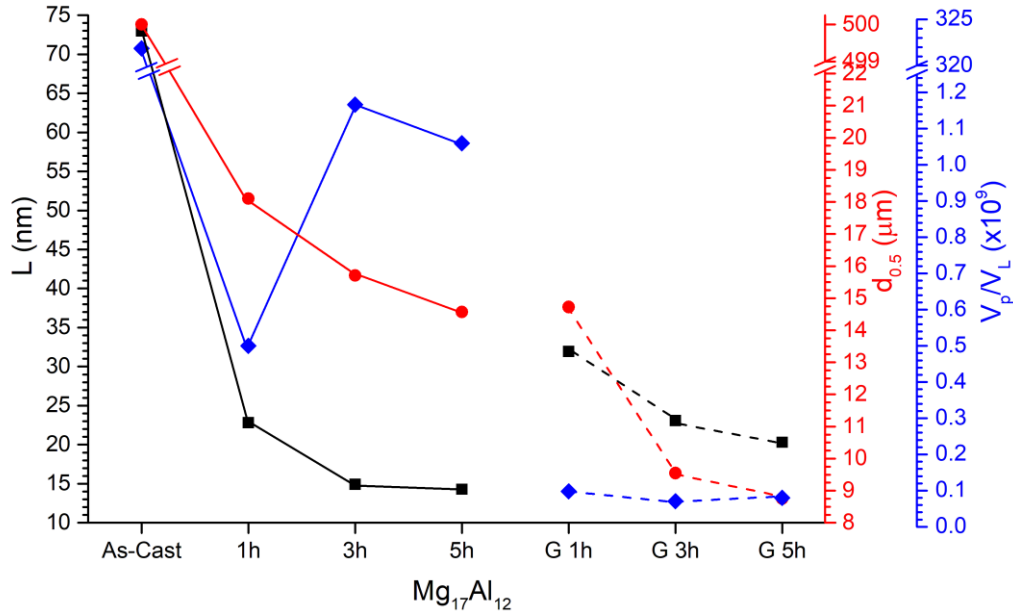


Figure 2: Variation of the crystallite size (L), the medium particles size ($d_{0.5}$) and the number of crystallite boundaries per particle (V_p/V_L) of as-cast $Mg_{17}Al_{12}$, $Mg_{17}Al_{12}$ after ball milling for 1h, 3h and 5h and $Mg_{17}Al_{12}$ after ball milling with graphite (denoted $Mg_{17}Al_{12} + G$) for 1h, 3h and 5h.

Crystallites size, denoted “ L ”, decrease from 74 nm to 23 nm after 1 hour of ball milling and barely decrease after 3h and 5h of ball milling (15 nm and 14 nm respectively) (figure 2). The medium (close to the average) particles size, denoted “ $d_{0.5}$ ”, decreased from 500 μm to 40 μm after 5h of ball milling (figure 2). Considering that defects may act as hydrolysis initiators sites [37], the average number of bulk defects in the milled material can be roughly estimated by dividing the particles volume by crystallites volume (denoted V_p/V_L). From this estimation, we consider that all defects are equivalent while actually, when particle size decreases, more surface defects are formed which are more efficient than bulk defects. Therefore, V_p/V_L value is better revealing when $d_{0.5}$ and L varies slightly (and or when $d_{0.5}$ is almost constant).

It is well known that ball milling is an effective way to create defects. Nevertheless, after 1h milling of $Mg_{17}Al_{12}$ the ratio V_p/V_L decreases (from 321×10^9 to 0.5×10^9) which could indicate that the number of defects is decreasing. This is mainly due to particles size reduction. Figure 2 shows this

ratio increases after 3h of milling to 1.2×10^9 indicating that more bulk defects are formed in addition to surface defects.

Figure 1 shows that increasing ball milling time enhances the hydrolysis performance of $Mg_{17}Al_{12}$. This is due to the destruction of the oxide layer formed on $Mg_{17}Al_{12}$ and to the decrease of crystallinity.

Ball milling reduces particles size and, therefore, increases the reactive surface area. The particle size decreases and the reactive area increases which improve the hydrolysis performance by favoring the dissolution of $Mg(OH)_2$. This phenomenon is described by the Noyes-Whitney equation [38] where the rate of dissolution of a solid is proportional to its surface area (considering the diffusion layer thickness, the diffusion coefficient, the concentration of $Mg(OH)_2$ in the bulk and in the diffusion layer as constants because the hydrolysis experiment is realized in the same conditions with the same NaCl solution).

3.3. Graphite addition

Ball milling with 5 wt. % of graphite improves the hydrolysis performance of Mg [23] and WE43 magnesium waste [13]. The effect of ball milling with graphite on the hydrolysis performance of $Mg_{17}Al_{12}$ was investigated by varying ball milling time (*i.e.* 1h, 3h and 5h) and graphite content (5 wt.% and 10 wt.%).

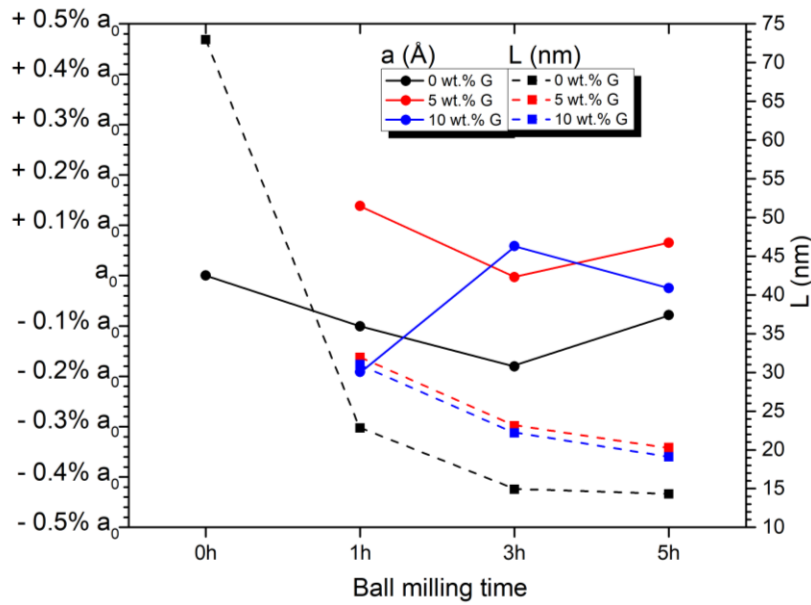


Figure 3: Variation of the unit cell parameter “a” (relative variation) symbolized by ● and the crystallite size “L” symbolized by ■ of the as-cast $Mg_{17}Al_{12}$, $Mg_{17}Al_{12}$ after ball milling without graphite (0 wt.% G), with 5 wt.% G and with 10 wt.% G for 1h, 3h and 5h.

As previously reported without G, the variation of the unit cell parameter (figure 3) is not significant since the maximum variation is 0.2%. Contrariwise, ball milling with graphite (5 wt.% and 10 wt.%) prevents the crystallite size reduction (figure 3). This phenomenon may be attributed to the lubricant effect of graphite [13, 23]. It is worth pointing out that increasing graphite content up to 10 wt.% does not change the crystallite size variation and consequently the materials reactivity. Based on these results, the addition of 5 wt.% of graphite was adopted while varying the ball milling time. Figure 2 shows that adding graphite during ball milling of $Mg_{17}Al_{12}$ promotes the reduction of particle size due to the anti-sticking effect of graphite [23] and subsequently decreases the crystallinity.

$Mg_{17}Al_{12}$ milled with graphite for 1h, 3h and 5h presents the same hydrolysis performance with a generation of 7% of the theoretical H_2 volume within 1 hour of reaction (Figure 1, e.g. $Mg_{17}Al_{12}$ milled for 5h produces 11% of the theoretical H_2 volume). That means that addition of graphite is not beneficial for the hydrolysis performance of $Mg_{17}Al_{12}$.

3.4. Chlorides addition

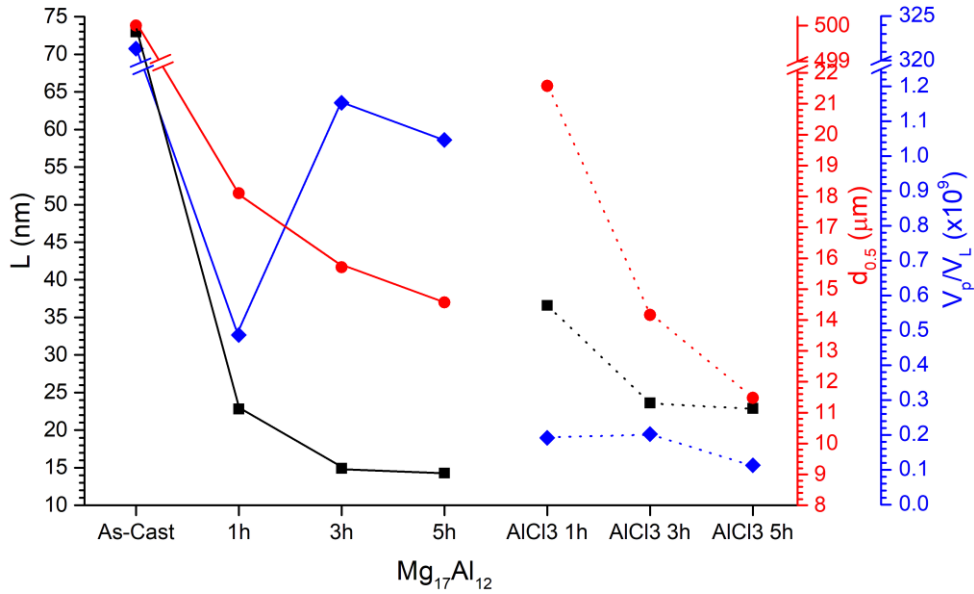


Figure 4: Variation of the crystallite size (L), the medium particles size ($d_{0.5}$) and the number of crystallite boundaries per particle (V_p/V_L) of as-cast $\text{Mg}_{17}\text{Al}_{12}$, $\text{Mg}_{17}\text{Al}_{12}$ after ball milling for 1h, 3h and 5h and $\text{Mg}_{17}\text{Al}_{12}$ after ball milling with AlCl_3 (denoted $\text{Mg}_{17}\text{Al}_{12} + \text{AlCl}_3$) for 1h, 3h and 5h.

Ball milling with AlCl_3 decreases particles size and crystallinity (figure 4). Increasing ball milling time with AlCl_3 from 1h to 5h reduces the particle size from 22 μm to 11 μm and the crystallites size from 40 nm to 25 nm respectively. Considering V_p/V_L ratio; the number of defects slightly decreases but it has to be considered that as the particles size decrease a lot, the number of surface defects will increase.

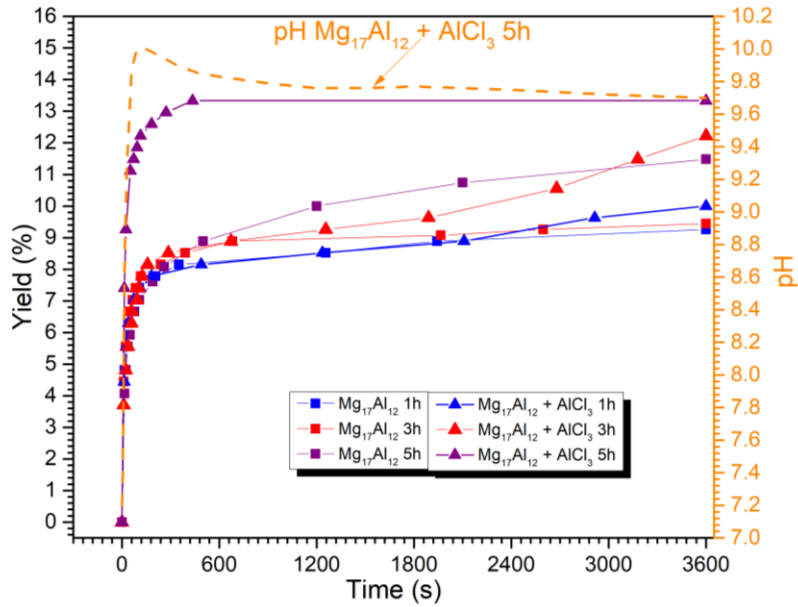
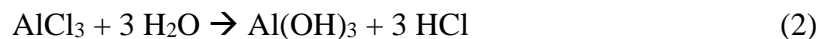


Figure 5: Hydrogen generation for hydrolysis with $Mg_{17}Al_{12}$ after ball milling for 1h, 3h and 5h and $Mg_{17}Al_{12}$ after ball milling with $AlCl_3$ (denoted $Mg_{17}Al_{12} + AlCl_3$) for 1h, 3h and 5h and pH monitoring during the hydrolysis of $Mg_{17}Al_{12} + AlCl_3$ 5h.

Figure 5 shows that adding $AlCl_3$ to $Mg_{17}Al_{12}$ enhances its hydrolysis performance – a maximum yield of 14% was obtained with $Mg_{17}Al_{12} + AlCl_3$ 5h. As seen from SEM analysis (figure 6), the presence of chlorides during ball milling creates cracks. It is known that the microstructural defects (*e.g.* cracks and crystallite boundaries) may act as hydrolysis initiators sites, withstand the continuous formation of the passive layer of $Mg(OH)_2$ [37], and enhance the pitting corrosion by the localized enrichment in chlorides [18]. Additionally, $AlCl_3$ is a strong water-absorbing agent and almost completely undergoes hydrolysis in water to generate chloride acid, which favor the dissolution of the formed $Mg(OH)_2$ [26, 39]. Indeed, the pH of the solution increases in the first 5 min of the hydrolysis reaction and reaches a value of 10 indicating the rapid formation of $Mg(OH)_2$. The exothermic dissolution of $AlCl_3$ increases the local temperature ($\Delta H = -223 \text{ kJ}\cdot\text{mol}^{-1}$) [26, 27] at the interface $Mg_{17}Al_{12}/H_2O$ and generates HCl through the following reaction [26]:



and shifts the final theoretical pH value from 10.8 (pH at the $Mg^{2+}/Mg(OH)_2$ equilibrium) to 9.7.

In fact, the pH of the solution can be calculated following the Henderson-Hasselbalch equation for a weak base:

$$\text{pH} = \text{pKa} + \log\left(\frac{S_0}{S - S_0}\right) \quad (3)$$

where S_0 is the molar solubility of the undissociated $\text{Mg}(\text{OH})_2$, S is the molar concentration of the dissociated $\text{Mg}(\text{OH})_2$ and pKa is that of $\text{Mg}^{2+}/\text{Mg}(\text{OH})_2$. When pH shifts to lower values, the solubility of $\text{Mg}(\text{OH})_2$ in the medium increases.

Based on our previous results, the reactivity of $\text{Mg}_{17}\text{Al}_{12}$ ball milled with MgCl_2 and NaCl for 5h was compared to that of $\text{Mg}_{17}\text{Al}_{12}$ ball milled 5h with AlCl_3 . It is well known that the presence of chlorides additives improves the efficiency of the milling process by creating microstructural defects and enabling the reduction of particles size thus increasing the surface area [33].

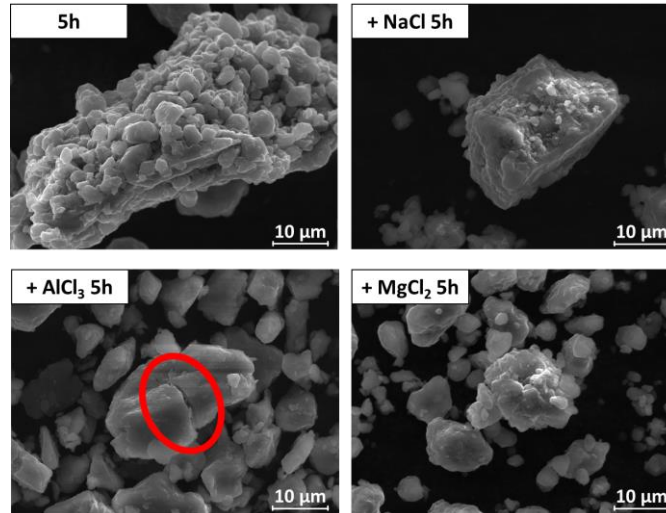


Figure 6: SEM images of $\text{Mg}_{17}\text{Al}_{12}$ 5h, $\text{Mg}_{17}\text{Al}_{12} + \text{NaCl}$ 5h, $\text{Mg}_{17}\text{Al}_{12} + \text{AlCl}_3$ 5h and $\text{Mg}_{17}\text{Al}_{12} + \text{MgCl}_2$ 5h.

As observed from SEM analysis (figure 6 and supplementary material figure 3), ball milling in the presence of AlCl_3 , MgCl_2 and NaCl for 5h slightly decreases the particles size favoring more fresh reactive $\text{Mg}_{17}\text{Al}_{12}$ surfaces (compared to $\text{Mg}_{17}\text{Al}_{12}$ 5h) . Cracks were also clearly observed in $\text{Mg}_{17}\text{Al}_{12} + \text{AlCl}_3$ 5h (e.g. red circle on figure 6 down left and supplementary material figure 3).

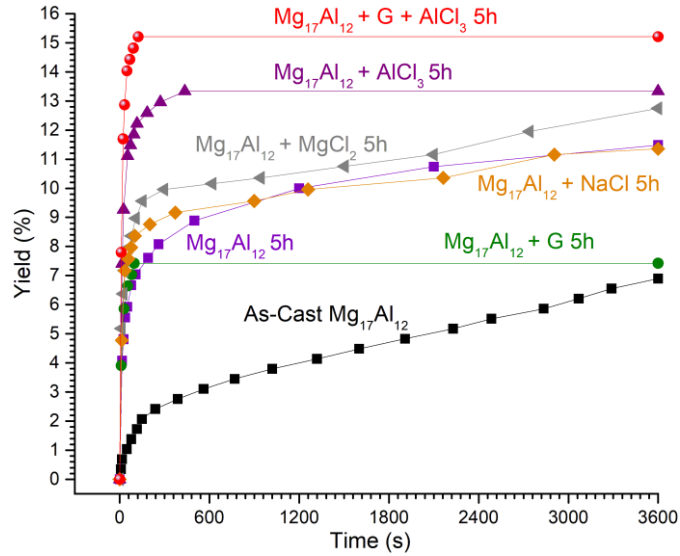


Figure 7: Hydrogen generation for hydrolysis with as-cast Mg₁₇Al₁₂, Mg₁₇Al₁₂ 5h, Mg₁₇Al₁₂ + G 5h, Mg₁₇Al₁₂ + AlCl₃ 5h, Mg₁₇Al₁₂ + MgCl₂ 5h, Mg₁₇Al₁₂ + NaCl 5h and Mg₁₇Al₁₂ + G + AlCl₃ 5h.

Addition of MgCl₂ leads to better hydrolysis performance of Mg₁₇Al₁₂ than addition of NaCl (Figure 7). These results may be attributed to the exothermic dissolution of MgCl₂ in the hydrolysis medium ($\Delta H = -155 \text{ kJ}\cdot\text{mol}^{-1}$) [27]. On the other hand, adding NaCl to Mg₁₇Al₁₂ does not favor its hydrolysis performance as NaCl dissolution is endothermic [27].

The effect of pH overrides the effect of the exothermicity of the dissolution of salts.

3.5. Synergetic effect of Graphite and AlCl₃

The addition of 5 wt.% of 2 additives (Graphite and Nickel) was found to enhance Mg [23] and WE43 [13] hydrolysis rate. Previously, we demonstrated that ball milling with AlCl₃ gives the best hydrolysis performance for Mg₁₇Al₁₂. Considering that the role of graphite and AlCl₃ are different in term of enhancing the hydrolysis reaction, the synergetic effect of graphite and AlCl₃ was studied.

Increasing ball milling time from 1h to 5h with addition of 5 wt.% of graphite and 5 wt.% of AlCl₃ improve the hydrolysis performance. Mg₁₇Al₁₂ + G + AlCl₃ BM 1h, 3h and 5 h generates 10%,

12% and 16% of the theoretical H_2 volume respectively (figure 7). Particles size and crystallinity of $Mg_{17}Al_{12}$ decrease when increasing ball milling time from 1h to 5h.

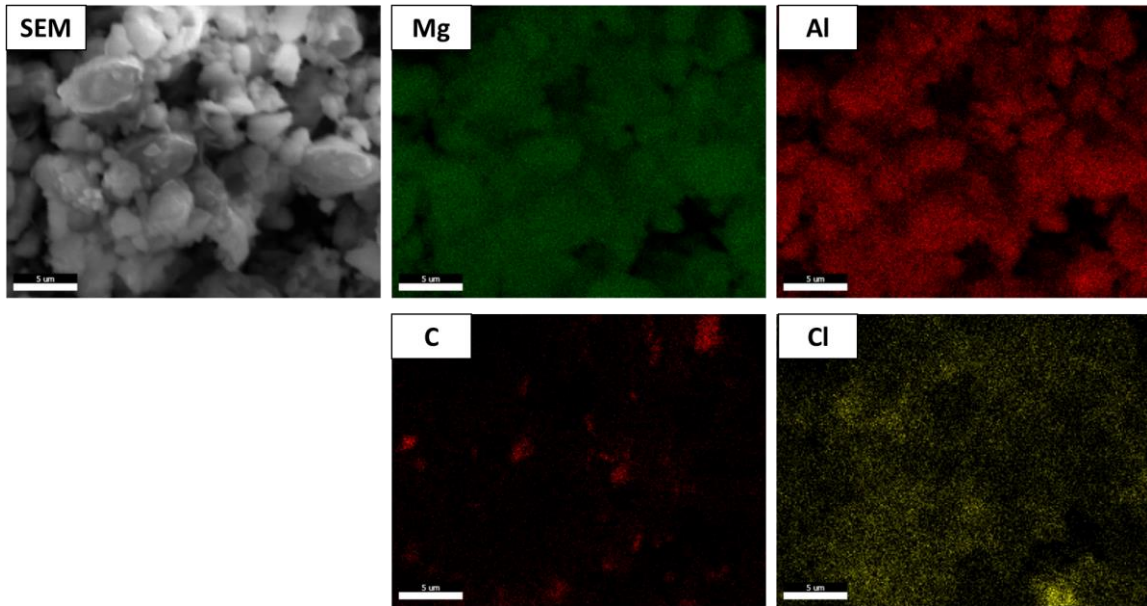


Figure 8 : SEM and EDX mapping of $Mg_{17}Al_{12} + AlCl_3$ 5h.

Figure 8 shows that graphite particles tend to agglomerate after prolonged ball milling (*i.e.* 5h). The same phenomenon was observed in a previous work [13]. Adding $AlCl_3$ reduces particles size and favor cracks formation (section 3.4) and graphite may form a fine protective layer on the fresh surface [13, 23].

It is worth pointing out that milling $Mg_{17}Al_{12}$ with graphite and $AlCl_3$ gives the best hydrolysis performance with a generation of 16% of the theoretical H_2 volume (which is almost triple that obtained for as cast $Mg_{17}Al_{12}$) within 1 hour of reaction.

4. Conclusion

In this work, the hydrolysis reaction of $Mg_{17}Al_{12}$ was investigated. The as-cast intermetallic produces 6% of the theoretical hydrogen volume. Ball milling was performed in order to enhance the hydrolysis performance. Increasing ball milling time to 5h improves the hydrolysis

performance with 11% reached in 1 hour. Upon all the tested additives (*i.e.* graphite, NaCl, MgCl₂ and AlCl₃), AlCl₃ showed the best performance with a generation of 14% of the theoretical hydrogen volume. This is attributed to the dissolution of AlCl₃, by generating HCl in the hydrolysis medium, which favor the dissolution of the formed Mg(OH)₂. Moreover, the extra heat released through the exothermic salt dissolution (*i.e.* MgCl₂ and AlCl₃) would also help to increase the yield and kinetics of the hydrolysis reaction. The addition of graphite and AlCl₃ simultaneously during ball milling of Mg₁₇Al₁₂ further enhances its hydrolysis with a generation of 16% of the theoretical H₂ volume. Based on our findings, a total hydrolysis of AZ alloys can not be achieved since, in the best case, 85% of Mg₁₇Al₁₂ does not react in 3.5 wt.% NaCl solution.

It is then worth pointing out that the hydrolysis of Mg₁₇Al₁₂ can be enhanced by ball milling with cheap additives such as graphite and AlCl₃. Subsequently, by following the same procedure (*i.e.* ball milling with additives), the hydrolysis of AZ magnesium alloys will be further improved. Therefore, this process can enable the low-cost production of pure hydrogen for fuel cells from magnesium alloys waste.

5. Acknowledgments

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6. Highlights

1. Mg₁₇Al₁₂ can produce hydrogen by the hydrolysis reaction
2. Ball milling with graphite and AlCl₃ are the best additives to improve Mg₁₇Al₁₂ hydrolysis.
3. Hydrolysis of Mg-Al alloys may be enhanced by ball milling with graphite and AlCl₃.

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