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Samuel Couillaud, Etienne Gaudin, Jérôme Andrieux, Stéphane Gorsse, Marion Gayot, et al.. Study of the hydrogenation mechanism of LaCuMg₈ ternary phase: the decomposition induces kinetics improvement. *International Journal of Hydrogen Energy*, 2012, 37 (16), pp.11824-11834. 10.1016/j.ijhydene.2012.05.025 . hal-00728221

HAL Id: hal-00728221

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Study of the hydrogenation mechanism of LaCuMg₈ ternary phase: The decomposition induces kinetics improvement

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Abstract

The hydrogen sorption properties of LaCuMg₈ are investigated. LaCuMg₈ crystallizes in the La₂Mg₁₇ structure type with the lattice parameters $a = 10.1254(2) \text{ \AA}$ and $c = 10.0751(2) \text{ \AA}$.

An absorption mechanism in 2 steps was reported earlier: (i) the first step, which is irreversible, induces the decomposition of LaCuMg₈ into an intimate mixture of 3 phases of submicronic size (*i.e.* LaH₃, MgCu₂ and MgH₂); (ii) the second step consists in the reversible absorption of the “LaCuMg₈ activated powder” with kinetics better than for pure magnesium. In order to get a better understanding of the absorption process, it was investigated from thermodynamic, kinetic and morphologic points of view. From thermodynamic point of view, the “LaCuMg₈ activated powder” behaves like a mixture. Concerning the kinetics, the activation energy was evaluated at about 65 kJ/mol H₂, using Avrami-Erofeev model and Arrhenius law. To explain the enhancement of the kinetics, both effects of (i) Mg₂Cu/MgCu₂ transformation and (ii) morphology induced by the decomposition have been considered.

Keywords: Rare-earth intermetallics, Hydrogen storage, Kinetic and thermodynamic study, Morphologic effects

1- Introduction

Magnesium is a promising candidate to store hydrogen in the solid state. It absorbs 7.6 wt% of hydrogen (wt% H₂), unfortunately with a low kinetics and at high temperature [1]. In order to decrease the absorption/desorption temperature, one way is to form binary compounds based on Mg. For example, Mg₂Ni [2,3] absorbs reversibly 3.6 wt% H₂ at 250 °C with an improved kinetics.

In the same way, the ternary compounds with magnesium are studied since few years [4-7]. For example, RENi₄Mg (with RE = La, Ce, Nd, Gd and Y), which crystallizes in cubic Laves phases, absorbs reversibly around 1 wt% of hydrogen at room temperature. Recently, a new ternary compound has been identified in the ternary system La-Cu-Mg : the so-called LaCuMg₈ [7]. This compound crystallizes in a disordered La₂Mg₁₇ structure type (S.G. P6₃/mmc) with the lattice parameters $a = 10.1254(2) \text{ \AA}$ and $c = 10.0751(2) \text{ \AA}$.

In the eighty's and ninety's, La₂Mg₁₇ has been studied for its hydrogen sorption properties [8-12]. In spite of the results of Dutta [12], with reversible capacity of 6.63 wt% H₂ (which are not confirmed), La₂Mg₁₇ absorbs reversibly a maximum of 3.1 wt% H₂ at 350 °C. During the first absorption step, La₂Mg₁₇ decomposes irreversibly into LaH₃ and MgH₂. For the following absorptions, the weight capacity is maintained and absorption becomes possible at 50 °C on Mg/MgH₂ couple (with however a slight decrease of the capacity with cycling).

In this paper, the hydrogen sorption mechanism of the LaCuMg₈ compound is studied in detail. Some similarities with La₂Mg₁₇ were observed. The reaction mechanism is in two steps (similar to La₂Mg₁₇) but the overall kinetics is enhanced by parameters like morphology and the transformation Mg₂Cu/MgCu₂.

The influence of the powder morphology and the transformation Mg₂Cu/MgCu₂ is discussed. Moreover, in order to improve the kinetics during the first step, effect of cold rolling on LaCuMg₈ is investigated.

2- Experimental details

Starting materials for the preparation of the samples with the initial composition 10La+10Cu+80Mg were lanthanum piece (Stream Chemicals, > 99.9 %), copper rod (Good Fellow, > 99.9 %) and magnesium rod (Alpha Aesar, > 99.8 %). To avoid oxides impurities, the surfaces of the magnesium and lanthanum pieces were carefully removed on a turning lathe. The pure metals were then weighted in the appropriate amounts and sealed in small

tantalum crucibles under an argon pressure of ca. 800 mbar. Before which the argon was purified using magnesium sponge (400 °C). Then, the crucibles were placed in a high frequency furnace under argon and heated at about 1100 °C and kept at this temperature for 2 min. The crucibles were then annealed in quartz tube under vacuum at 400 °C for two weeks. Finally the tubes were quenched to room temperature. No reaction with the tantalum tubes was observed. The polycrystalline samples were stable in air.

One part of the as-cast compound was inserted between two stainless steel plates and rolled in air in a conventional rolling mill with 75 mm diameter rolls. Before each roll, the sample was folded in two and during rolling the thickness was reduced by about 50%. The as-prepared samples were stored in air before hydrogen activation and sorption measurements.

All polycrystalline samples were characterized ex-situ with X-ray powder diffraction using a Philips PW 1050 diffractometer with CuK α radiation ($\lambda_{K_{\alpha 1}} = 1.5406 \text{ \AA}$, $\lambda_{K_{\alpha 2}} = 1.5443 \text{ \AA}$). These patterns were scanned by steps of 0.02° (2θ) from 5° to 80° with a constant counting time of 30 s. They were analyzed by full patterns matching using the FULLPROF program [13].

In-situ synchrotron X-ray diffraction experiments were performed on beamline ID15B of the European Synchrotron Radiation Facility in Grenoble. The X-ray beam size was 0.3 (V) x 0.4 (H) mm² and the X-ray energy (wavelength) was 87.07 keV ($\lambda = 0.1424 \text{ \AA}$) using a single-bounce Si(511) bent Laue monochromator. On ID15, it is possible to perform powder X-ray diffraction experiment in transmission mode using the high pressure high temperature gas loading system (HPHTgls). Powder samples were loaded in the reaction cell (fused silica, i.d. = 3 mm, w.t. = 0.5 mm) under inert atmosphere. The gas loading system was used to apply on the sample either an argon flow of 500 ml.min⁻¹ (dehydrogenation step) or a hydrogen static pressure of at least 30 bar (hydrogenation step). The sample can be heated up to 300 °C at 10 °C.min⁻¹ (dehydrogenation step) or cooled down to ambient temperature from 300 °C at 10 °C.min⁻¹ (hydrogenation step). X-ray diffraction rings from the samples were collected at ~1000 mm using a 2D flat panel detector (Pixium Trixell 4700). The exposure time for each acquisition was 1.2 s (sum of 3 images of 0.4 s) and acquisition was collected every 10 s. It is to note that more information about the ID15's HPHT gas loading system can be found elsewhere [14].

The bulk samples were investigated ex-situ by electron probe microanalyses (EPMA with metallic La, Ni, Cu and Mg, as standards). The bulk samples were embedded in a

methylmetacrylate matrix and the surface was polished with different silica and diamond pastes. The surface remained unetched for the EPMA measurements.

The morphology of powders after absorption was observed by scanning electron microscopy (SEM). SEM micrographs were acquired using a Tescan VEGA II-SBH working at 10 and 20 kV with a current beam of 90 μ A.

Hydrogen sorption kinetics were investigated by the use of an automatic Sievert-type volumetric apparatus (HERA, Hydrogen Storage System) in the temperature range from room temperature to 330 °C and with 10 bar of H₂ [15].

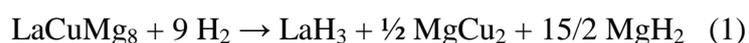
3 – Results and discussion

3-1 Study of the hydrogenation mechanism of LaCuMg₈

The preliminary results obtained on LaCuMg₈ have shown a hydrogen sorption mechanism in two steps [7,16].

3-1-a First step reaction : Activation step

During the first step, LaCuMg₈ is irreversibly decomposed into LaH₃, MgH₂ and MgCu₂ according to the reaction given below:



In previous papers [7,16], an absorption around 2 wt% H₂ at 300 °C under 10 bar in 19 hours was reported. In fact, a more precise investigation with better experimental conditions on this first absorption leads to a weight capacity of 3.2 wt% H₂. Even if this capacity is closer to the theoretical capacity (*i.e.* 4.53 wt% H₂), the difference between the experimental measurement and the theoretical value is still not fully explained. The rapid formation of LaH₃ could be proposed as a hypothesis. Indeed, if the formation of LaH₃ is done during filling of the reservoir, this reaction is not measured. Consequently, the theoretical gravimetric capacity should be decreased at 3.8 wt% H₂.

Nevertheless, the kinetics of the first absorption is still very slow as the absorption is complete after more than one day. In the following, this first step will be called “activation process”. According to the literature, it is possible to increase the activation process by cold

rolling [17,18]. For example, Dufour et al.[17] showed that after cold rolling, the activation kinetics of Mg_6Pd was increased. In order to evaluate the effect of cold rolling on $LaCuMg_8$, the as-cast compound was cold rolled 20 and 150 times in air. The hydrogen sorption kinetics at 300 °C and 10 bar of H_2 are plotted in figure 1. After 20 cold rolls, the hydrogen storage capacity is like as-cast compound but the absorption is comparatively quicker and is completed in 3h. For the sample cold rolled 150 times, an almost similar kinetics is observed but the capacity decreases strongly to about 1.3 wt% H_2 . The decrease of the hydrogen storage capacity can be explained by the oxide formation (observed by EPMA analysis) which increases with cold rolls number as the cold rolling is done under air. The increase of strain introduced by cold rolling could also affect the maximum capacity [19]. However, we have shown that the strain is maximum after 20 rolls and decreases after. Therefore, the maximum storage capacity should be higher for the sample rolled 150 times rather than for the one rolled 20 times. Then, if the effect of strain can not be neglected, the oxidation phenomenon seems to play the major role. According to this result, the kinetics of activation step is 9 times quicker by cold rolling. However, the kinetic improvement is only observed for the first absorption and no effect on the subsequent hydrogen sorption cycles was noticed. It is even possible to observe a slight decrease of the capacity because of the oxide formed during cold rolling.

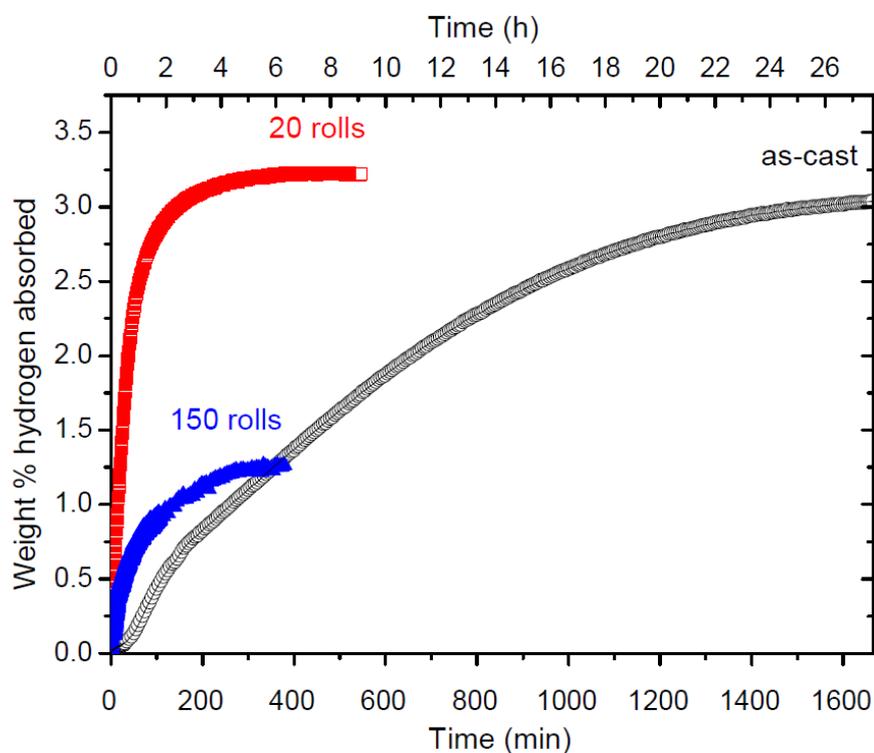
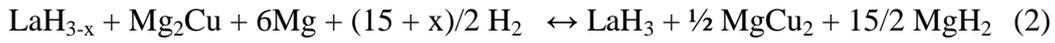


Figure 1 : Hydrogen absorption kinetics under 10 bar of H_2 and 300 °C, for $LaCuMg_8$ as-cast (black circle) and for $LaCuMg_8$ cold-rolled 20 (red square) and 150 times (blue triangle).

3-1-b Second step reversible reaction:

During the second step a maximum reversible capacity of 3.3 wt% H₂ was obtained at 300 °C and 30 bar [7,16].

It is now established that the reversible reaction at 300 °C can be written:



In order to study this reaction, several absorptions were made at different temperatures. All of these sorptions are reported in figure 2.

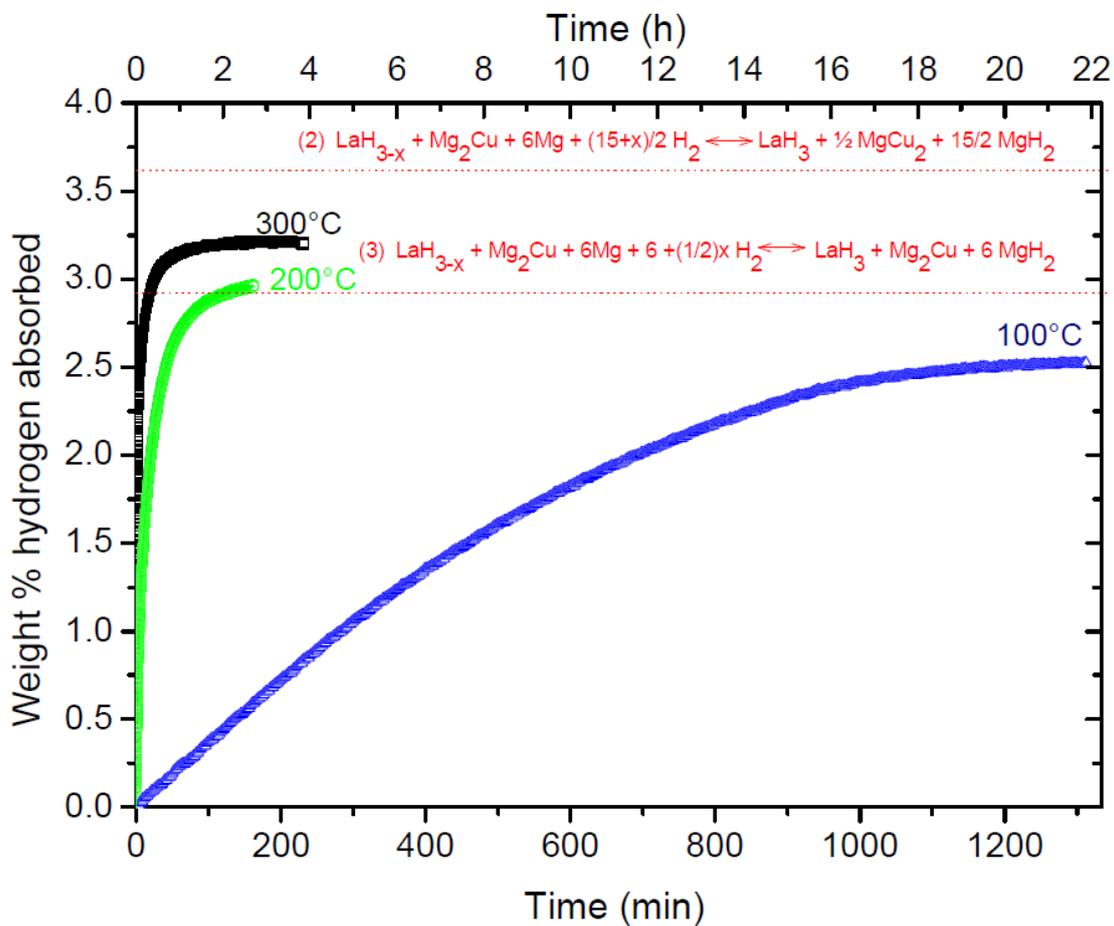


Figure 2: Hydrogen absorption kinetics for "LaCuMg8 activated powder" under 10 bar of H₂ and 100 °C (blue triangle), 200 °C (green circle) and 300 °C (black square). The dashed lines show theoretical hydrogen uptakes according to reaction (2) and (3), of 3.6 wt% and 2.9 wt% respectively.

At 300 °C, the second absorption is complete in less than 30 minutes. At 200 °C, the kinetics decreases slightly but the hydrogen storage capacity remains almost unchanged. At 100 °C, the kinetics decreases again and the maximum amount of hydrogen absorbed is lower. This last point can be explained by the mechanism which changes below 200 °C. Indeed, according to XRD pattern obtained after absorption at 100 °C, the following reaction can be proposed:



This observation is in good agreement with the previous work of Reilly [20] which explains the conversion reaction $\text{Mg}_2\text{Cu}/\text{MgCu}_2$ under hydrogen even if the temperature of this transformation was reported only at around 300 °C.

The desorption curves at 280 °C and 300 °C are given in figure 3. At 300 °C, about 3 wt% H_2 is desorbed in 25min. So the reversibility is complete and faster than for pure magnesium powder. At 280 °C, 2.5 wt% is desorbed in 1 hour. The so-called “LaCuMg₈ activated powder” allows obtaining magnesium powders which store hydrogen with a better kinetics and a lower reversibility temperature than the pure magnesium [21, 22]. In order to get a better understanding of the sorption behavior, the “LaCuMg₈ activated powder” was studied from thermodynamic, kinetic and morphologic point of view.

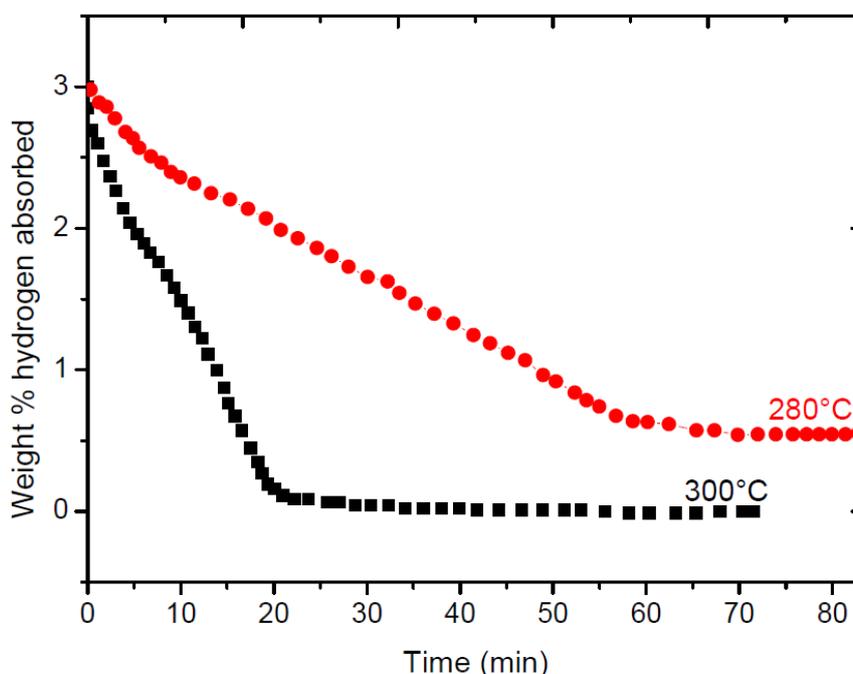


Figure 3: Hydrogen desorption for “LaCuMg₈ activated powder” under 0.2 bar of H_2 and 280 °C (red circle) and 300 °C (black square).

3-2 Thermodynamic study of the sorption reaction

The thermodynamic properties of this mechanism were studied, using PCT curves and theoretical calculation. The PCT curves at 300 °C and 350 °C are given in figure 4.

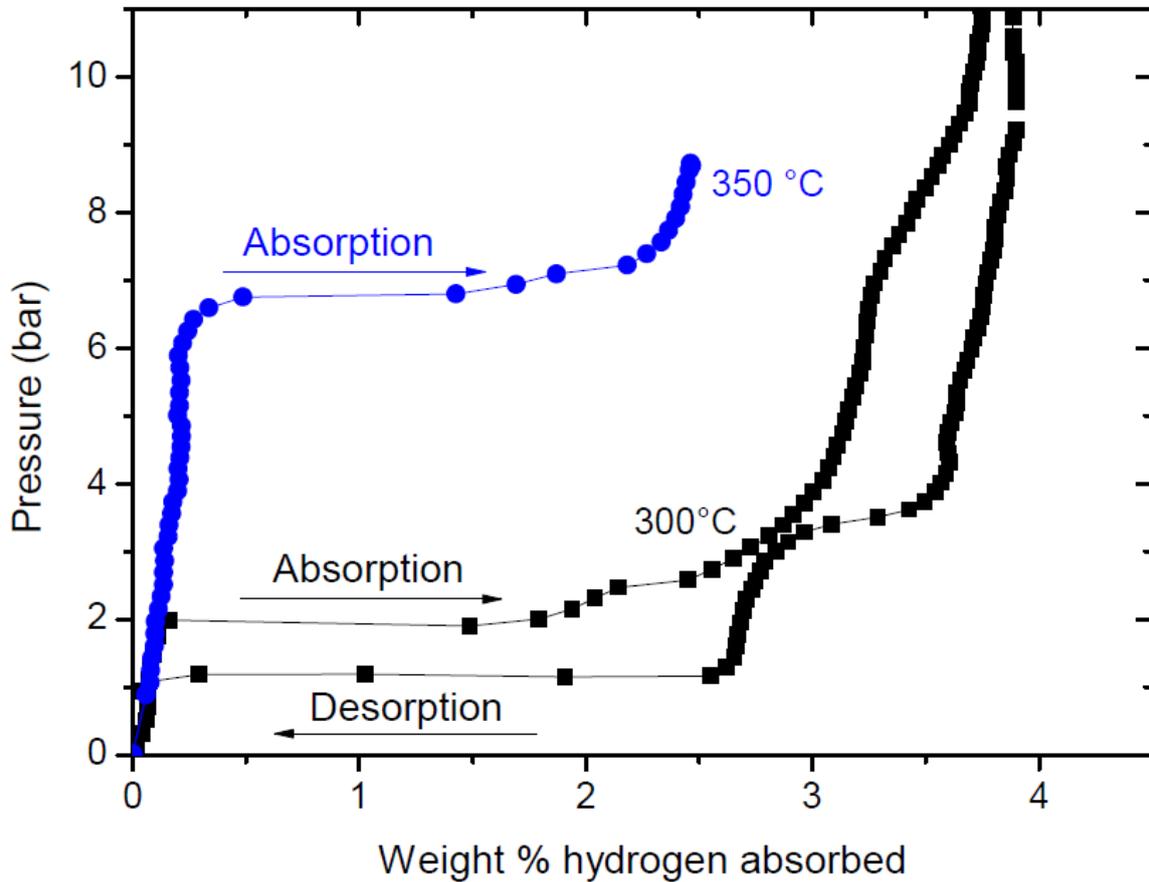
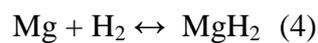


Figure 4 : PCT curves of “LaCuMg8 activated powder” under hydrogen at 300 °C (black square) and 350 °C (blue circle).

Thermo-Calc software was used to calculate equilibrium temperatures under different hydrogen pressures for the absorption of the mixture Mg + Mg₂Cu which is separate into two steps as follows:

- (i) the first is related to the reaction of pure magnesium with hydrogen.



- (ii) the second corresponds to the reaction between Mg₂Cu and hydrogen.



The Gibbs energy parameters of the phases involved in chemical reactions were taken from CALPHAD assessments of Mg-H [23] and Cu-Mg [24] systems. The calculated Van't Hoff plot for Mg and Mg₂Cu are reported in Figure 5.

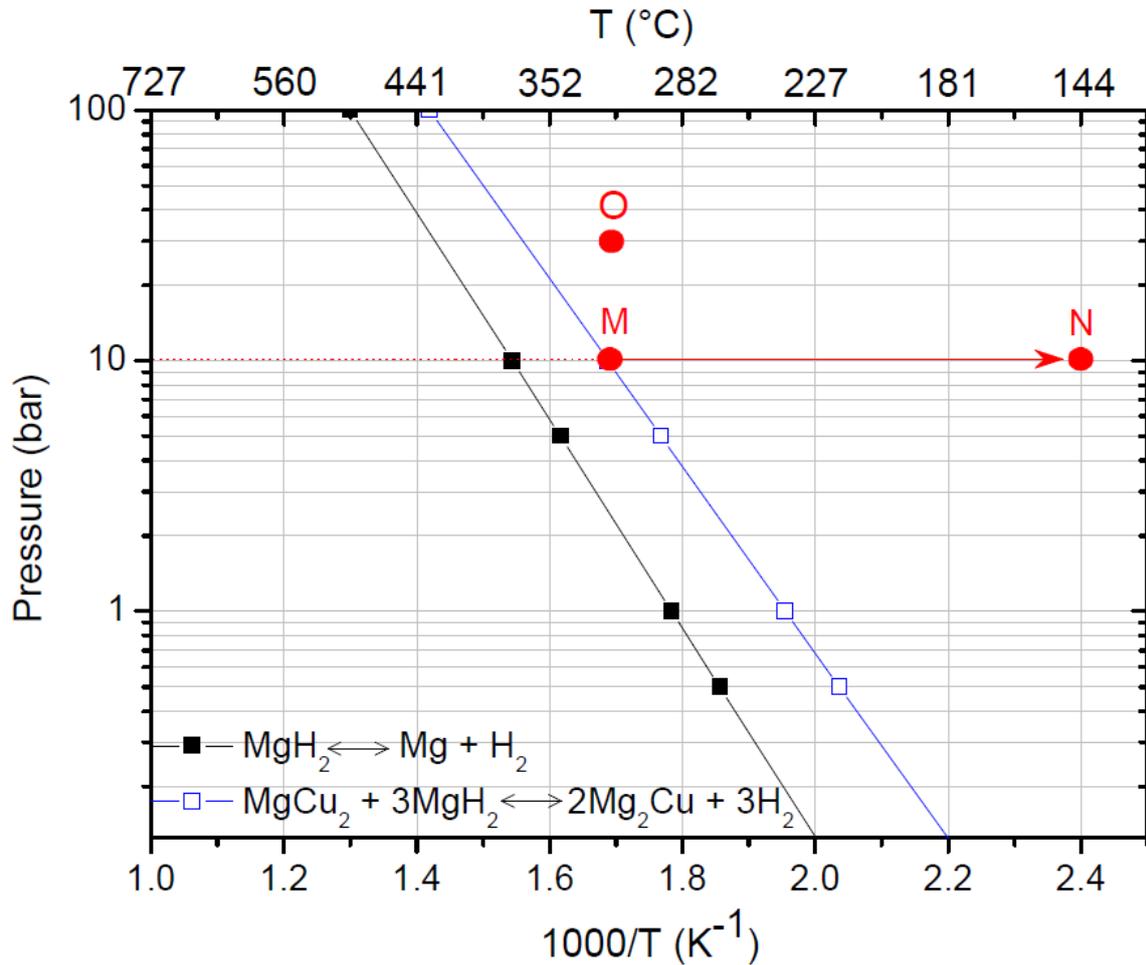


Figure 5 : Calculated Van't Hoff plots of the various reactions for the destabilization of magnesium hydride.

From experimental point of view, at 300 °C, during absorption, one plateau pressure is observed around 2 bar and one can be expected between 7 and 10 bar with an important slope (figure 4). This last one is confirmed by the desorption curve on which the experimental conditions allow a better resolution. During desorption, the plateau pressures are observed around 1 bar and 3.5 bar. So, between absorption and desorption curve a large hysteresis is observed especially for the higher plateau pressure.

At the same temperature, it is indicated from the thermodynamic calculation that the first plateau pressure might be around 1.5 bar and the second one might be at 6 bar (figure 5).

The theoretical pressures are at the center of the experimental hysteresis, which indicates a relative good agreement.

In the same way, at 350 °C, the pressure of the first equilibrium increases to about 7 bar in accordance with the theoretical pressure (*i.e.* 6 bar). The second plateau cannot be observed with our experimental conditions (*e.g.* limitation of the apparatus) and consequently the desorption could not be started.

The good agreement between theory and experience demonstrates that this simple thermodynamic calculation is an efficient tool to describe the reaction in the system Mg-Cu-H. Nevertheless, the presence of LaH₃, which could affect the reaction, is not considered in this thermodynamic calculation. So, the first experimental plateau pressure corresponds to the reaction (4) and the second to the reaction (5). According to reactions (4) and (5), the hysteresis on the first plateau is unexpected. Indeed, the actual results reported show a hysteresis on magnesium hydride only above 400 °C [25]. As a consequence, the LaCuMg₈ decomposition leads to a magnesium powder which should be slightly different from a microscopic point of view. This point will be addressed in section 3.4-b.

According to the thermodynamic calculation, the equilibrium of the transformation Mg₂Cu/MgCu₂ (reaction 5) is at 315 °C, under 10 bar of hydrogen (figure 5, point M). When the temperature decreases (from point M to N, figure 5), the thermodynamic driving force of the reaction (5) increases and the transformation should be easier. This result is in disagreement with the hydrogenation mechanism observed for “LaCuMg₈ activated powder”. Indeed, below 200 °C the transformation Mg₂Cu/MgCu₂ is not observed. This point can be explained by the competition between the thermodynamic and the kinetic parameters: in the temperature range 200 °C ≤ T ≤ 300 °C, the system is in thermodynamic equilibrium while, when the temperature decreases (≈ 100 °C), the kinetic parameter becomes the limiting factor.

3-3 Study of the second step reaction by in-situ synchrotron X-Ray diffraction

In order to improve understanding of absorption and desorption mechanism, “LaCuMg₈ activated powder” has been studied by in-situ synchrotron X-Ray diffraction. The powder previously decomposed and hydrogenated (*i.e.* end of the activation cycle) has been gradually heated up to 300 °C (10 °C/min) under argon flux (figure 6), maintained for 5 min at 300 °C under 30 bar of H₂ and gradually cooled from 300 °C to 100 °C (10 °C/min) (figure 7).

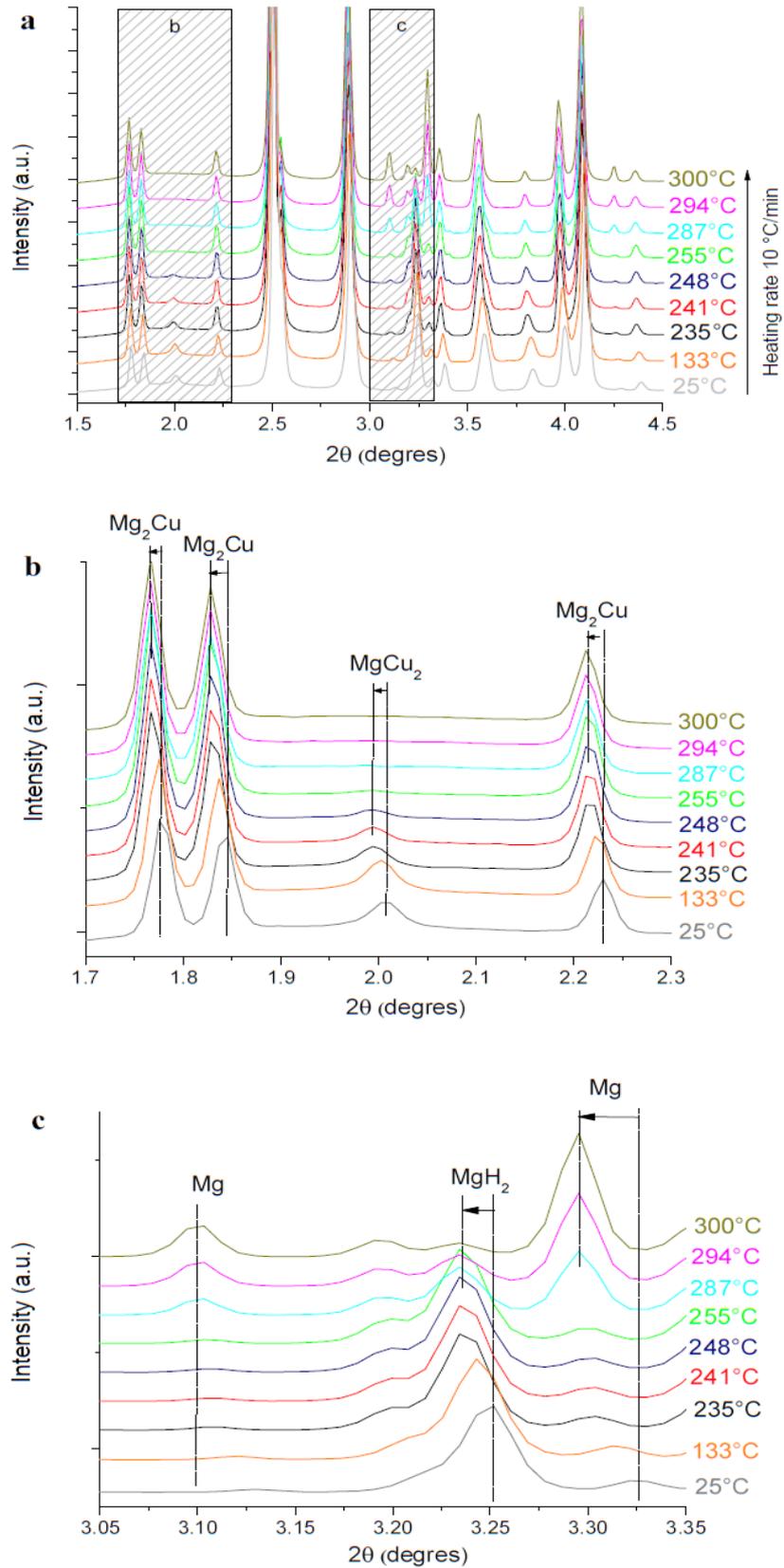


Figure 6 : In-situ synchrotron X-Ray diffraction of “LaCuMg8 activated powder” during the desorption step (from 25 °C to 300 °C at 10 °C/min) under argon flow (500 mL.m⁻¹). The figure b and c are the enlarged portions of figure a indicated by hatched zones.

The X-Ray pattern at 25 °C (figure 6) shows that hydrogenation during decomposition was not complete leading to the coexistence of MgCu₂ and Mg₂Cu phases. This point can be explained by :

- (i) the increase of the sample weight (*i.e.* 3 times more than results presented in part 3-1) for the same experimental conditions (*i.e.* 300 °C/10 bar). In this case, the experimental conditions might be not sufficient to lead to the total Mg₂Cu/MgCu₂ conversion;
- (ii) or by a transformation Mg₂Cu → MgCu₂ more difficult to achieve than expected from the thermodynamic calculation.

During the desorption (figure 6), the MgCu₂ phase disappears between 248 °C and 255 °C and in the same times, the quantity of Mg₂Cu phase increases as seen from the intensity of the peaks at 2 and 2.22 °(2θ) respectively (figure 6.b). Between 287 °C and 300 °C, the MgH₂ phase is dehydrogenated (figure 6.c). The LaH₃ phase remains unchanged during the desorption (not shown here). It is to be noted that both transformations are complete at 300 °C. The shift observed between the X-Ray patterns at low temperature and the X-Ray patterns at high temperature was explained by the lattice expansion due to the increase in temperature. At the end of the heating step, three phases were observed in equilibrium at 300 °C: LaH₃, Mg₂Cu and Mg. This experiment agrees well with the desorption mechanism given in the part 3-1.

Insertion of H₂ in the reactor at 300 °C induced rapid reaction with magnesium to form MgH₂ phase (figure 7).

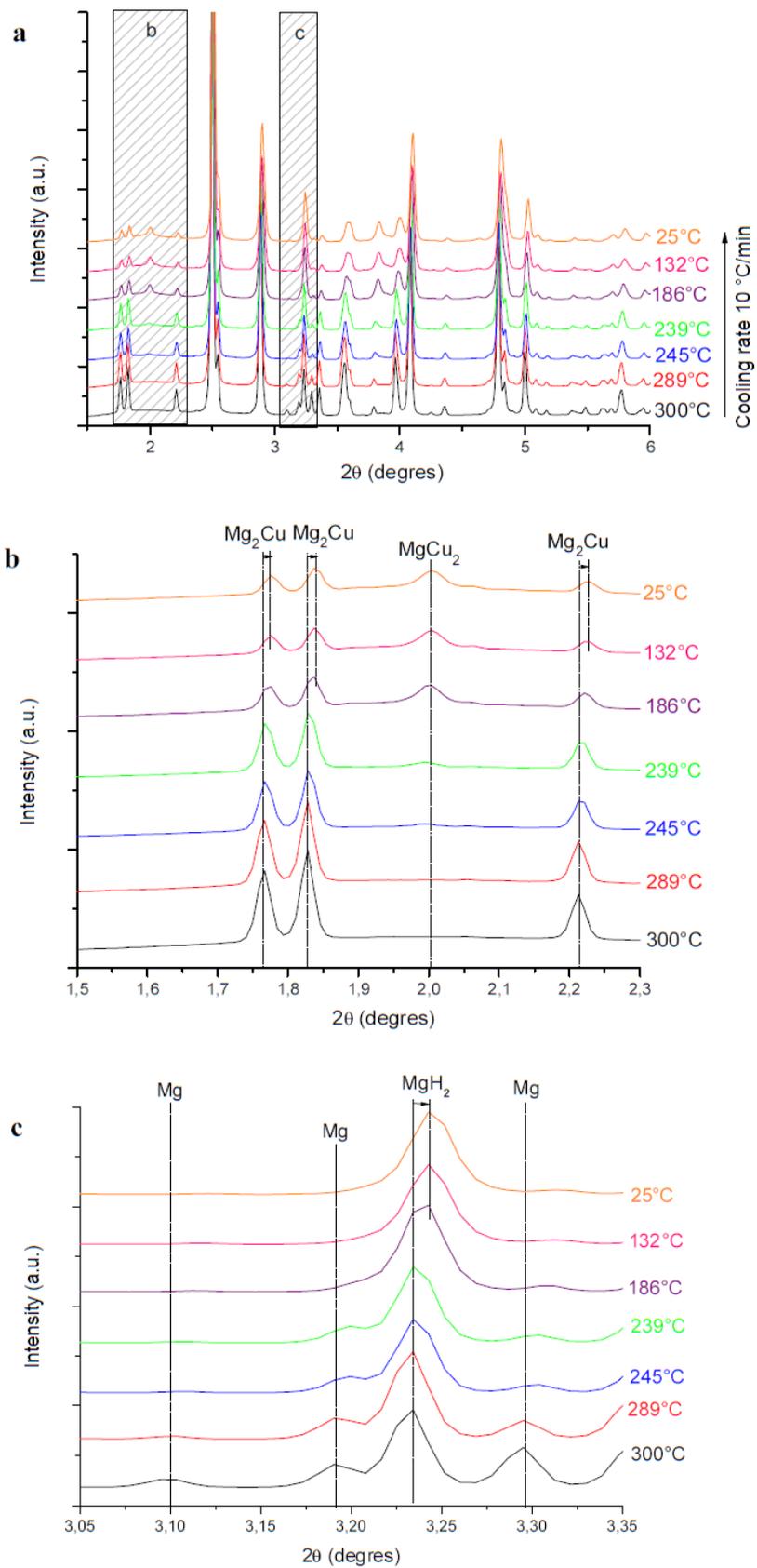


Figure 7 : In-situ synchrotron X-Ray diffraction of “LaCuMg8 activated powder” during the absorption step (from 300 °C to 25 °C at 10 °C/min) under 30 bar of hydrogen. The figure b and c are the enlarged portions of figure a indicated by hatched zones.

Around 239 °C, this reaction was completed (figure 7.c) and between 245 °C and 186 °C, the reaction between Mg_2Cu and H_2 to form $MgCu_2$ phase occurred (figure 7.b). Below 186 °C, the X-Ray patterns remain unchanged but the transformation $Mg_2Cu/MgCu_2$ was not complete. This experiment highlights several interesting points:

- 1- At 300 °C, the reaction of Mg with H_2 was almost instantaneous which shows that the magnesium in the system called “LaCuMg₈ activated powder” has better kinetic than pure magnesium.
- 2- At 300 °C, the transformation $Mg_2Cu \rightarrow MgCu_2$ did not occur. This point disagrees with the thermodynamic calculation. Indeed, at 300 °C under 30 bar of H_2 (point O in the figure 5), one could expect that the transformation $Mg_2Cu/MgCu_2$ occurs. One explanation could be that the experimental conditions were near the thermodynamic equilibrium. In this case, the thermodynamic driving force was not sufficient. However, even if this hypothesis is validated, the results disagree with our ex-situ observations discussed in part 3-1.
- 3- At the end of the cooling step under 30 bar of hydrogen, the transformation $Mg_2Cu \rightarrow MgCu_2$ was not complete. Two hypotheses can be proposed to explain this point :
 - (i) The transformation was blocked. The same phenomenon was observed and described previously for the initial powder. However, according to the intensity of the diffraction peaks on figure 6b and 7b, the ratio $MgCu_2/Mg_2Cu$ increases in comparison with the initial powder;
 - (ii) The decrease of the temperature slows down and finally stops the transformation. Indeed, according to our ex-situ observation discussed in part 3-1, the transformation did not occur at 100 °C. Around 100-150 °C, the kinetic factor might become the limiting step and stops the reaction in a non equilibrium state.

To conclude our neutron studies, the transformation $Mg_2Cu/MgCu_2$ seems to be the limiting factor in the reaction between “LaCuMg₈ activated powder” and hydrogen.

3-4 Study of hydrogenation kinetics mechanism of LaCuMg₈

In order to complete the comprehension of the hydrogenation mechanism of LaCuMg₈, the absorption kinetics were studied using Avrami–Erofeev equation [26, 27]. The absorption rate is controlled by different mechanisms which are responsible for the different trends observed on curve. At the beginning of the absorption reaction a surface process, a chemisorption process and a nucleation process appear, in order to form the hydride (β phase) [28]. When the hydride is formed completely, the diffusion of hydrogen through the hydride layer constitutes the determining step [29, 30]. The reaction mechanism was analysed by Avrami-Erofeev equation in the domain $0.2 \leq F \leq 0.8$ following eq.6.

$$F = 1 - \exp(-kt^n) \quad (6)$$

Where F is the fraction of hydrogen absorbed and desorbed, k is the reaction rate constant for a given temperature and n is the reaction order.

Avrami-Erofeev equation can be rewritten :

$$\ln[-\ln(1-F)] = \ln(k) + n \times \ln(t) \quad (7)$$

In order to determine the k values, the curves $\ln[-\ln(1-F)]$ were drawn at each temperature. Each curve can be linearized. The slope of the linearization is related to n , and the value at the origin to k . For example the curves obtained at 300 °C and 100 °C are given in figure 8.

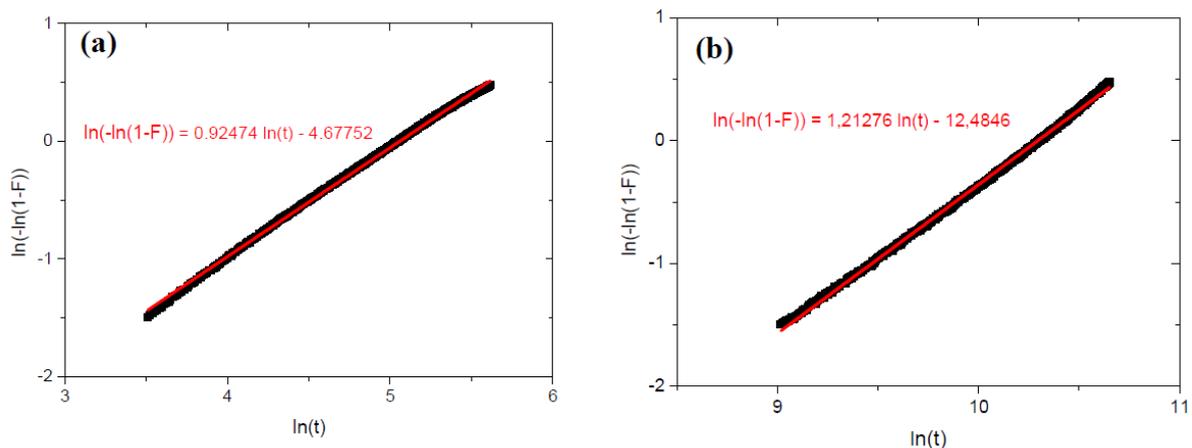


Figure 8 : $\ln(-\ln(1-F))$ versus $\ln(t)$ plot for the absorption kinetics at 300 °C (a) and 100 °C (b) of “LaCuMg₈ activated powder”.

From the values of reaction rate constant k at different temperatures, the activation energy was determined using Arrhenius law (equation 8).

$$k = k_0 \exp(-E_a/RT) \leftrightarrow \ln(k) = -E_a/RT + \ln(k_0) \quad (8)$$

An activation energy of $E_a = 66 \text{ kJ/mol H}_2$ has been obtained from the slope of $\ln(k)$ versus $1/T$ plot (figure 9).

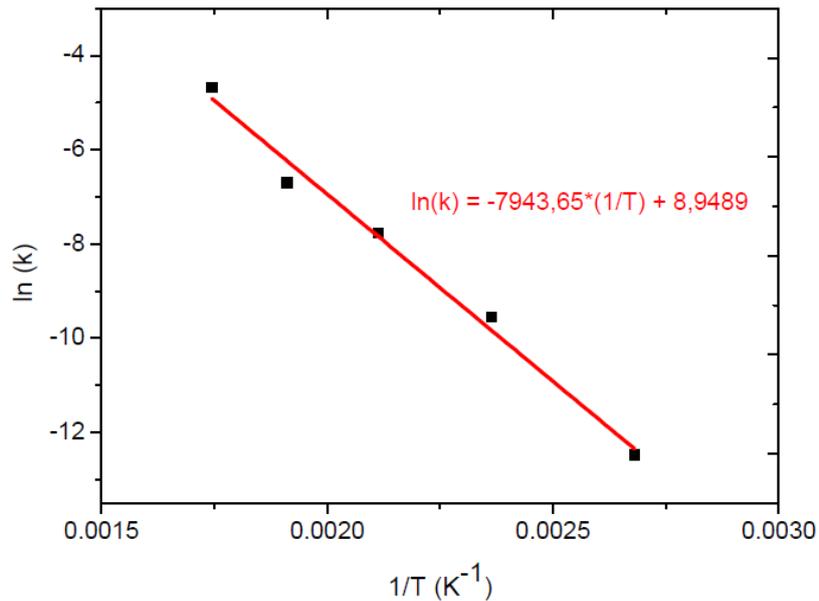


Figure 9 : Arrhenius plot for the determination of the activation energy of “LaCuMg8 activated powder”.

In the case of pure magnesium, the activation energy reported is around 110-120 kJ/mol H_2 [31]. This value can be decreased for magnesium ball milled under hydrogen. The activation energy is even lower for Mg doped with catalytic elements. For example, the activation energy varied from 62 to 90 kJ/mol H_2 for Mg doped with transition elements [32] and is equal to 51 kJ/mol H_2 for Mg doped with Cr_2O_3 oxide [28]

As our activation energy (66 kJ/mol H_2) was about two times lower than for pure magnesium and in the same order than catalyzed and milled magnesium systems, this study demonstrates the interest of the La-Cu-Mg ternary system.

3-4 Parameters which could improve the kinetic properties

Several hypotheses could be suggested to explain the kinetic improvements. The catalytic effect of LaH_3 and Mg_2Cu , the effect of the transformation $\text{Mg}_2\text{Cu}/\text{MgCu}_2$ or the effect of the decomposition of LaCuMg_8 during the first absorption step are three key points to improve the kinetics. Their influences are discussed in the following.

3-4-a Catalytic effects

Catalytic effects of Mg_2Cu have been already reported in the literature [33-35]. Indeed, Karty *et al.* [33] have shown that Mg_2Cu phase limits the oxidation of magnesium surface. The dissociation and diffusion of hydrogen are not limited by an oxide layer and the kinetics are improved. The absorption kinetics at 100 °C (figure 2), which was better than the absorption kinetics of pure magnesium at higher temperature confirms the catalytic effect of Mg_2Cu phase.

At high temperature, we demonstrated that Mg_2Cu reacts with hydrogen to form MgCu_2 . During one hydrogen cycle (absorption and desorption), Mg-Cu bonds are broken and created. This mechanism induces, after each cycle, the formation of “clean” atoms of magnesium (*i.e.* without oxygen on the surface). The scheme proposed in figure 10 illustrates this effect on numerous cycles. We suggest that the transformation $\text{Mg}_2\text{Cu}/\text{MgCu}_2$ allows maintaining the reactivity of powder and, consequently, enhances the sorption kinetics. In order to validate this hypothesis, the cycling stability is still under progress.

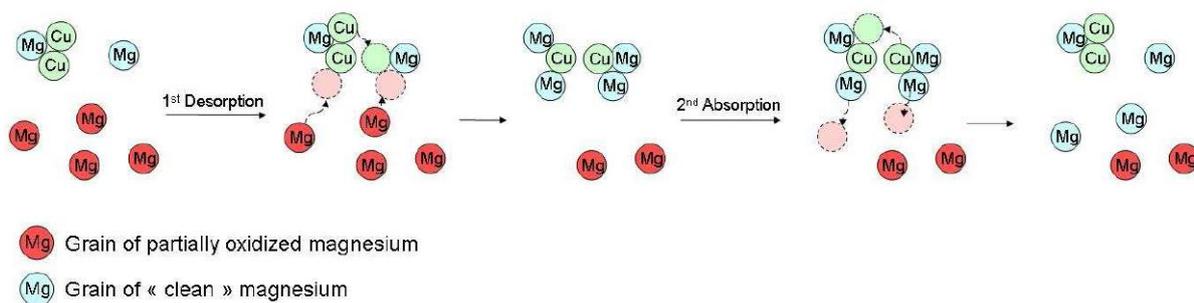


Figure 10 : Scheme describing the mechanism of the transformation $\text{Mg}_2\text{Cu}/\text{MgCu}_2$ during sorption cycles.

However, even if a catalytic effect can be considered, the kinetics observed for “LaCuMg₈ activated powder” are better than the mixture Mg + Mg₂Cu studied by Andreasen *et al.* [34] (table 1).

Table 1: Comparison between the mixture MgH₂+MgCu₂ of Andreasen work’s [32] and our “LaCuMg₈ activated powder” for absorption and desorption.

	%wt hydrogen absorbed/ theoretical %wt hydrogen (%)	Temperature (°C)	Time (h)	Ref
Absorption	93	325	12	[32]
	89	300	1	Our work
Desorption	88	360	6	[32]
	92	300	0.41	Our work

This mixture, obtained by ball milling, absorbs and desorbs hydrogen with slower kinetics and at higher temperature. Moreover, the activation energy calculated for this mixture was $E_a = 108$ kJ/mol H₂ (which is higher than the “LaCuMg₈ activated powder” *i.e.* 66 kJ/mol H₂). Regarding this comparison between data from literature and our work, other parameters has to be considered to explain kinetic improvements (*e.g.* morphologic effect).

3-4-b Morphologic effect induced by the decomposition

The powder morphology during absorption and desorption at different steps was studied by scanning electron microscopy (SEM) and presented in the figure 11.

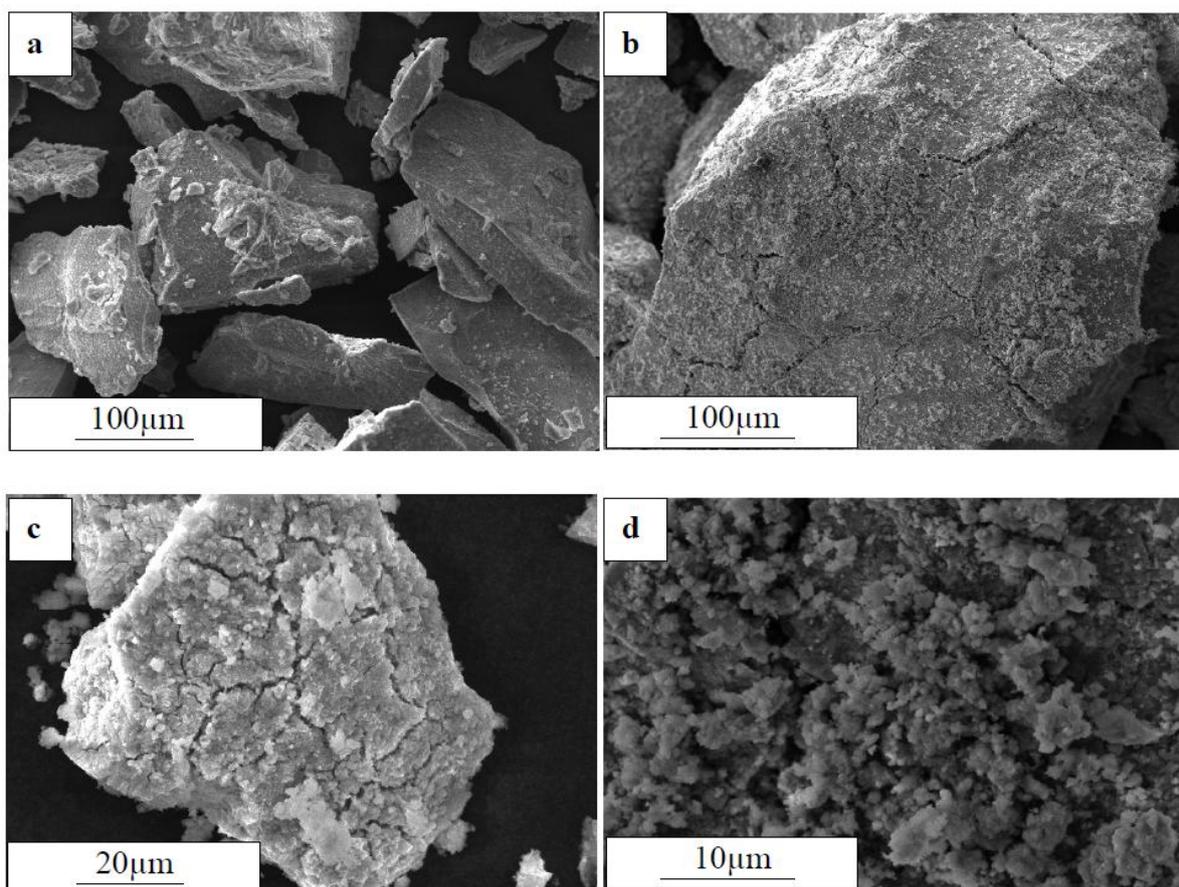


Figure 11 : SEM pictures (secondary electron) of “LaCuMg₈ activated powder” after decomposition (a) and after 4 absorption/desorption cycles (b, c, d).

After decomposition (figure 11.a), the powder shows a irregular shape and its surface is smooth. The particles size varies from 50 μm to 200 μm . After four hydro/dehydrogenation cycles at 300 $^{\circ}\text{C}$ (figure 11.b-d), the size and the global shape of grains seem unchanged even if small particles appear on the grains surface. The size of these particles can be estimated around 2-5 μm . However, numerous cracks appear. The cracks lead to new fresh surface without oxygen pollution (i.e. passivation layer) for the adsorption-dissociation step. The absorption should be easier and faster. This effect is already reported in several works where the authors reduce the grain size or use decrification phenomenon to increase the surface for the adsorption-dissociation step and so to increase the kinetics [22, 36, 37]. Moreover, as magnesium has a high ductility, no cracks have been already observed for pure magnesium. The cracks, observed in figure 11.b-d indicate a decrease of the ductility of “LaCuMg₈ activated powder”. This could only be explained by the formation of a heterophase inside the magnesium grain. In order to confirm this point, the chemical composition of several grains after four hydro/dehydrogenation cycles has been determined by EPMA with WDS detector.

The distribution of each element inside one grain (representative of global sample) is given in figure 12.

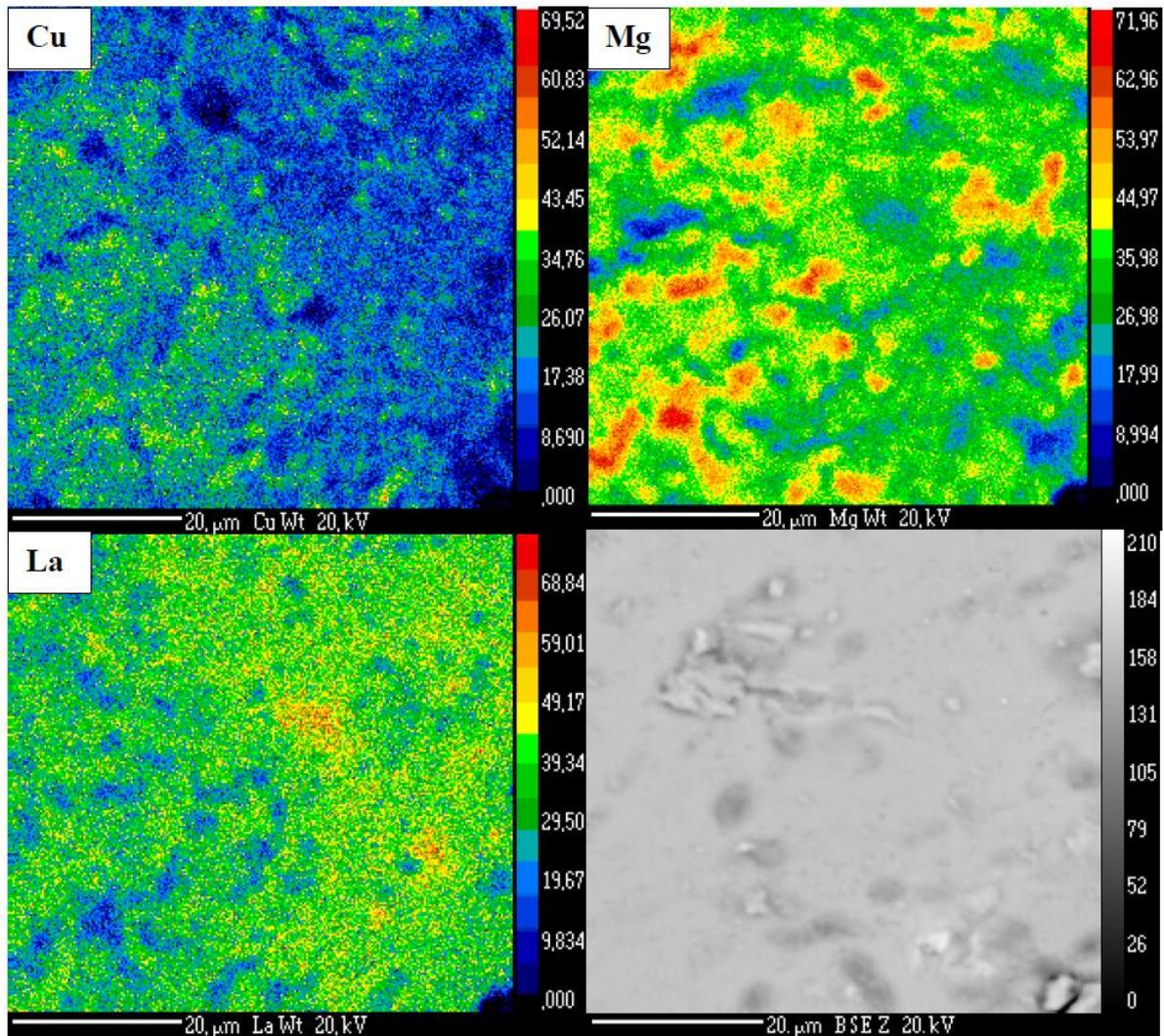


Figure 12: EPMA analysis of one grain of “LaCuMg₈ activated compound” after four absorption/desorption cycles. The three first pictures represent the repartition of one element (i.e. Cu, Mg, La) inside the grain. The last one is the BSE picture.

Magnesium, copper and lanthanum are observed inside the same particle. The repartition of lanthanum and copper is globally homogeneous. However, the domains which contain more lanthanum are poorer in copper and magnesium. The domains enriched in copper are also enriched in magnesium, what highlight the binary Mg-Cu. According to figure 12, the LaH₃, Mg₂Cu and Mg phases can be observed and their sizes can be estimated around micrometre range. It is now established that the decrease of grain size allows increasing the absorption kinetic [37]. The sub-micronic size and the intimate mixture of the 3 phases obtained by the decomposition of LaCuMg₈ under hydrogen allow improving absorption kinetics without the use of long ball milling process or the addition of catalyst. Even if

lanthanum has a negative effect on gravimetric hydrogen storage, it is necessary to lead to the decomposition and as a consequence to obtain a good kinetics.

It is to note that, Au *et al.* [38] and Karty *et al.* [33] propose an effect of Mg/Mg₂Cu interface on the dissociation and the diffusion of hydrogen. According to the sub-micronic size of each phase on the “LaCuMg₈ activated powder”, interfaces between Mg and Mg₂Cu are a key point in the morphological effect. Even if this point has not been highlighted in our study, it has to be considered to explain the improvement of the sorption kinetics.

4-Conclusion

The sorption properties/mechanism of the LaCuMg₈ compound was studied with attention. This compound is irreversibly decomposed during the first absorption at 300 °C and under 10 bar of H₂. Consequently, an intimate mixture of LaH₃, MgH₂ and MgCu₂ which can be considered as the real storage material is obtained. In order to improve the slow kinetic (≈ 19 h) the cold rolling was used. After only 20 cold rolls, the activation time is strongly decreased (≤ 3 h).

After decomposition, the powder stores hydrogen with good kinetics and lower temperatures than pure magnesium. The absorption reaction changes according to the temperature. At a temperature higher than 200 °C, Mg and Mg₂Cu react with hydrogen while, below 100 °C, only the magnesium reacts with hydrogen. The appropriate thermodynamic calculation on the system Mg-Cu-H confirms the experiments data. According to the kinetic study, an activation energy of about 66 kJ/mol H₂ has been determined for “LaCuMg₈ activated powder” using the Avrami-Erofeev equation. Therefore, combining both results on thermodynamic and kinetics, an effect of transformation Mg₂Cu/MgCu₂ to explain the good kinetics has been proposed. Indeed, after each cycle, this transformation induces the formation of “clean” atoms of magnesium. Nevertheless, from the in-situ synchrotron study, it appears that this transformation is difficult to achieve and its optimization would lead to an increase of the hydrogen sorption properties. To finish, an EPMA analysis on the “LaCuMg₈ activated powder” shows that the decomposition leads to grains (50-200 μm) composed by an intimate mixture of 3 phases with a sub-micronic size. This special morphology obtained without the use of long ball milling process is one of the parameters to increase the absorption kinetics and is the key point of the interest of our approach about alloying magnesium to lanthanum and copper.

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