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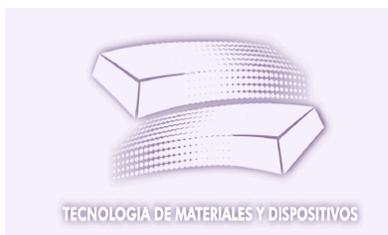
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Abstract: The transition metal complex hydride Mg_2FeH_6 has been successfully synthesized utilizing mechanical milling of a 2Mg-Fe mixture followed by heating at 673 K under 6 MPa of hydrogen pressure, without pressing step. The obtained yield of Mg_2FeH_6 was about 50%. Hydrogen storage properties of the Mg-Fe-H system, i.e. capacities, absorption/desorption kinetics and thermodynamic parameters, were examined. The pressure-composition isotherm (PCI) measurements of the samples at 548-673 K showed that the alloys possessed good cyclic stability and reversibility. Enthalpies and entropies of decomposition of the Mg-Fe-H system were evaluated by van't Hoff plots. The absorption /desorption rates at 573 K were very fast in comparison with the reported data. The non-isothermal desorption of hydrogen was found greatly dependent on the thermal history of the sample.



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Please find attached a copy of the manuscript entitled: “**Thermodynamic and kinetic studies of Mg – Fe – H after mechanical milling followed by sintering**”, by J. A. Puszkiel, P. Arneodo Larochette and F. C. Gennari to be considered for publication in the *Journal of Alloys and Compounds*.

The main subject of this work is focused on the understanding of thermodynamics and kinetics of Mg – Fe – H system obtained via synthesis of an elemental 2Mg – Fe mixture. The synthesis method consisted of mechanical milling followed by hydriding at high temperature and pressure.

The presented results contribute mainly to the knowledge of thermodynamic and kinetic behaviour of Mg – Fe – H system. The thermodynamic characterization was carried out in a wide range of temperature (548 – 723 K), while kinetic studies were performed at 573 K and a pressure range between 1.3 and 5.2 MPa. Regarding to the applied synthesis method, we successfully produced Mg₂FeH₆, which is one of the not well characterized complex hydrides with potential hydrogen storage applications. We also improved the sintering procedure avoiding the pressing step used in former works. Some of the obtained results have not been reported in previous publications yet.

The manuscript, or its contents in some other form, has not been published previously by any of the authors and/or is not under consideration for publication in another journal at the time of submission.

Hoping the manuscript meets the editorial requirements.

Sincerely yours

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Prime Novelty Statement

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Thermodynamic and kinetic studies of Mg – Fe – H after mechanical milling followed by sintering

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ABSTRACT

The transition metal complex hydride Mg_2FeH_6 has been successfully synthesized utilizing mechanical milling of a 2Mg-Fe mixture followed by heating at 673 K under 6 MPa of hydrogen pressure, without pressing step. The obtained yield of Mg_2FeH_6 was about 50%. Hydrogen storage properties of the Mg-Fe-H system, i.e. capacities, absorption/desorption kinetics and thermodynamic parameters, were examined. The pressure-composition isotherm (PCI) measurements of the samples at 548-673 K showed that the alloys possessed good cyclic stability and reversibility. Enthalpies and entropies of decomposition of the Mg-Fe-H system were evaluated by van't Hoff plots. The absorption /desorption rates at 573 K were very fast in comparison with the reported data. The non-isothermal desorption of hydrogen was found greatly dependent on the thermal history of the sample.

1. INTRODUCTION

Hydrogen is an excellent energy carrier to be used in both fuel cells and combustion engines as a clean fuel. However, the application of hydrogen technology presents many problems that have not been solved yet. One of the major problems is hydrogen storage. Metal hydrides provide a safe and efficient alternative for hydrogen storage applications. Most of the metal hydrides investigated derive from pure metals, intermetallic compounds and alloys [1,2]. They present metallic properties and are traditionally called “interstitials” since they have been considered as solid solutions of hydrogen in the interstitials of metals, alloy or intermetallic matrixes. Although there have been several attempts to produce metal hydrides with better properties, disadvantages such as their low gravimetric hydrogen content, problems associated with their regeneration and high temperature needed for hydrogen desorption have not been improved much. Then, the challenge in the field of hydrogen storage is the development of new

materials which can fulfill the following requirements: high volumetric-gravimetric capacity, good hydrogen hydriding-dehydriding properties, optimum kinetics at reasonably low temperatures and low degradability under thermal or pressure cycling. Complex metal hydrides form a subclass of metal hydrides that have been scarcely studied and appear as potential materials for hydrogen storage [3,4]. These compounds are stoichiometric and usually nonmetallic; they are known as “complex” due to the presence of discrete metal-hydrogen ligands in the crystal structure. Among all complex hydrides, the Mg_2FeH_6 shows the highest known volumetric hydrogen density of $150 \text{ kg H}_2\cdot\text{m}^{-3}$ and has a high gravimetric hydrogen density of 5.47 wt%, resulting in a promising hydrogen storage material. However, this ternary hydride has the particularity that Mg and Fe do not form stable binary compounds between themselves [5]. As a consequence of this, the synthesis of Mg_2FeH_6 is difficult to carry out. Then, several investigations associated with Mg_2FeH_6 have been oriented to enhance the hydride yield [6-16]. Only one work has studied in detail thermodynamic properties [13] and few characterizations of the hydriding / dehydriding kinetics have been reported [8, 16].

Several procedures have been explored to produce Mg_2FeH_6 [6-16]. In 1984, Mg_2FeH_6 was first synthesized from a mixture of 2Mg-Fe by a process known as sintering, which consists of hydriding previously pressed powders at high temperatures ($\sim 793 \text{ K}$) and pressures ($\sim 12 \text{ MPa}$) during 10 - 20 days [6]. In a subsequent investigation [8], these experimental conditions were optimized to allow the production of Mg_2FeH_6 as nearly a single-phase (9 MPa and 723 K); however, some amount of iron remained unreacted. Further works introduced mechanical milling (MM) or MM in combination with other steps to improve the synthesis of Mg_2FeH_6 [9-12, 14-16]. One procedure consists of milling elemental Mg and Fe in an inert atmosphere (e. g. Ar), pressing the powders mixture to conform a pellet and then sintering it at high pressure and temperature [9]. Huot *et al.* have reported the formation of Mg_2FeH_6 through MM of 2Mg-Fe under argon or hydrogen atmosphere followed by sintering (623 K under 0.5 MPa of H_2), obtaining a hydride yield of 21 wt% under argon and 65 wt% under hydrogen atmosphere [9]. Other ways to synthesize Mg_2FeH_6 are mainly based on MM of 2Mg-Fe mixture under hydrogen atmosphere (reactive mechanical alloying, RMA) [11, 12, 15] and MM of 2MgH_2 -Fe mixture in an inert atmosphere or under hydrogen atmosphere [10, 14, 16]. The yield of Mg_2FeH_6 produced by RMA or MM depends on both the starting materials and the milling conditions.

The difficulties associated with the synthesis of Mg_2FeH_6 and the impossibility to obtain a pure hydride sample, are likely the main reasons for the limited knowledge about the thermodynamic equilibrium and the rate approaching the equilibrium of the Mg-Fe-H system at low temperatures ($\leq 673 \text{ K}$).

In this work we investigate the Mg_2FeH_6 synthesis from a 2Mg-Fe mixture after MM, and its thermodynamic and kinetic properties. Complex hydride Mg_2FeH_6 synthesis was performed via mechanical milling followed by sintering at 673 K and under 6 MPa of hydrogen during 15 h, without pressing step or cycling. Pressure-composition-isotherm (PCI) plots provided information about practical properties of the system (reversibility and equilibrium pressure) and thermodynamic data at temperatures lower than 673 K (heat of hydrogen absorption/desorption). The characterization of the kinetics behavior showed good absorption rates at 573 K associated with the MgH_2 - Mg_2FeH_6 mixture.

2. EXPERIMENTAL

2.1. Synthesis of Mg_2FeH_6

Elemental Mg powder and Fe chips (purity higher than 99%) were mechanically milled under argon atmosphere, using a magneto - mill Uni-Ball-Mill II (Australian Scientific Instruments). The Mg powder had an agglomerate size distribution between 400 μm and 150 μm (estimated via scanning electron microscopy) and its surface looked smooth (Fig. 1A). The Fe granules had an agglomerate size $> 1\text{mm}$ (Fig. 1B). The effect of the starting material size on the material properties evolution during mechanical milling was studied. A stoichiometric 2Mg-Fe mixture together with ferromagnetic steel balls were placed in a stainless steel container and enclosed in an argon dry box. The samples were milled for 100 h, at a rotation speed of 180 rpm. The ball to powder weight ratio was 44:1. At 2 h and 100 h the container was opened to collect a sample for analysis. All material handling was carried out in a glove box with controlled atmosphere. The powder mixture obtained after 100 h of milling was used as starting material for the sintering process, according to the reference [7]. Two important modifications to the standard sintering procedure were applied: the pressing step was avoided and the hydrogen pressure during the hydriding process was kept constant in a selected value. Based on these changes, the 2Mg-Fe mixture milled 100 h was subjected to hydrogenation at 673 K under 6 MPa of hydrogen pressure during 15 h. Hydrogen absorption was performed using a modified Sieverts device [17] where the system pressure was set by means of a mass flow controller.

2.2. Characterization

The crystalline structure of as-milled samples and hydriding powder were characterized by X-ray diffraction (XRD) analysis on a Philips PW 1710/01 Instruments with $\text{CuK}\alpha$ radiation (graphite monochromator). The crystallite size was calculated using the Scherrer equation. The Mg-Fe distribution was studied by scanning electron microscopy (SEM 515, Philips Electronic Instruments) on resin-mounted and polished powders. The thermal behavior was investigated by differential scanning calorimetry (DSC) using a TA 2910 calorimeter at a heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$ and an argon flow rate of $122\text{ ml}\cdot\text{min}^{-1}$. The proportion of MgH_2 and Mg_2FeH_6 was calculated from the DSC curves, using the peak area and the heat of formation of MgH_2 ($67\text{ kJ}\cdot\text{mol}^{-1}$) and Mg_2FeH_6 ($80\text{ kJ}\cdot\text{mol}^{-1}$), reported in this work.

Pressure-composition isotherms (PCIs) and hydrogen absorption kinetics were measured using a modified Sieverts-type device coupled with a mass flow controller [17] (same equipment used for complex hydride synthesis). Absorption/desorption PCIs were performed after first hydrogen absorption at 673 K, starting from 548 K to 648 K. Then, the sample was kept at 673 K under dynamic vacuum during 6 h, and PCIs from 673 K to 723 K were obtained. The equilibrium plateau pressure was calculated as an average of the experimental points in the plateau region, taking into account the error propagation theory in order to assign an error range to each calculated equilibrium pressure. The kinetics of the system was studied by heating up the sample to the reaction temperature and kept at this temperature for 30 min before beginning a hydrogen absorption / desorption measurement.

3. RESULTS AND DISCUSSION

3.1. Preparation of Mg_2FeH_6 : mechanical milling followed by sintering

According to the binary phase diagram of Mg-Fe, a known intermetallic or stable compound between Mg and Fe does not exist; hence Mg and Fe are practically not miscible [5]. Figure 2 shows the XRD patterns of the 2Mg-Fe mixture after 100 h of milling under argon atmosphere. In agreement with the binary phase diagram, no formation of new phases between Mg and Fe was observed during the milling process. The Mg diffraction peaks (JCPDS Powder Diffraction Data Card N° 35-0821) became smaller and broader after 100 h of milling (in comparison with 2 h of milling, not shown), as a direct consequence of the crystallite size reduction and/or the plastic deformation. A significant reduction in Mg crystallite size from

>1000 nm (starting material) to 35 nm (100 h of milling) was determined using the Scherrer equation. As regards of Fe diffraction peaks (JCPDS Powder Diffraction Data Card N° 06-0696) shown in figure 2, the Fe crystallite size was also reduced from 1000 nm to 32 nm after 100 h of milling. No further structural changes, such as MgO formation (JCPDS Powder Diffraction Data Card N° 45-0946), were observed after 100 h of milling. The distribution of Mg and Fe phases was observed with backscattered electrons (Fig. 2A and 2B). The bright phase corresponds to Fe, and the dark one to Mg. After milling for 2 h, big Fe particles can be clearly identified in Fig. 2A. These particles were not easily incorporated into the Mg matrix. Repeated cold welding and fracturing during 100 h caused a significant reduction in the iron agglomerates size, producing the refinement of the microstructure. This process favored the dispersion of the Fe particles within the Mg matrix. Even though the big starting chips of Fe were substantially reduced and progressively incorporated into the Mg matrix during the milling process, in Fig. 2B Fe particles of 30-40 μm can be observed.

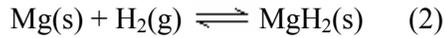
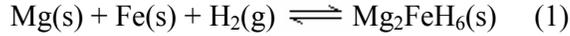
The 2Mg-Fe mixture milled for 100 h was used as starting material to investigate the thermodynamics and kinetics of the Mg-Fe-H system. The as-milled sample without pressing was put into a reactor and subjected to 6 MPa of hydrogen pressure at 673 K during 15 h (see §2). The first hydrogen absorption rate is shown in Fig. 3A. A striking result is that most hydrogen consumption occurred during the first 6 h. The measured hydrogen storage capacity in the hydriding process was about 4.5 wt%. Considering that the maximum capacity of hydrogen storage in the system 2Mg-Fe is 5.47 wt% for the complete Mg_2FeH_6 formation and about 3.6 wt% for the total Mg hydriding, the reaction after 15 h at 673 K and 6 MPa involved a partial complex hydride synthesis. To clarify the nature of the hydrides formed during the hydrogen absorption process, Fig. 3B shows the pressure-composition desorption isotherm at 673 K of as-synthesized Mg-Fe-H hydrides. Hydrogen desorption occurs in two stages given by well-defined plateaus at 1530 kPa and 780 kPa. An X-ray diffraction pattern of the material at the lower plateau region in the 673 K isotherm (arrow in Figure 3B) shows the presence of Mg_2FeH_6 , Mg and Fe as main phases (Figure 4A). Then, the upper plateau can be associated with MgH_2 decomposition and the lower plateau with that of Mg_2FeH_6 . The relative amounts of these hydrides were 18 wt% and 49 wt%, respectively. Minor differences between the total hydrogen capacities obtained from Figures 3A and 3B can be related with differences in the experimental conditions given by kinetic or thermodynamic constrains.

To clarify the analysis, we classify the synthesis procedures reported in the literature in two wide groups: sintering (the traditional procedure), and MM (performed under different

atmospheres and experimental conditions). We refer to sintering as those processes that involve previous stages (pressing, milling and/or cycling) followed by a thermal treatment at high temperature and hydrogen pressure. In the case of MM, we include in this group those synthesis methods that only use MM under Ar or H₂. A summary of the composition and nature of the starting materials, experimental conditions and total hydrogen capacity is presented in Table I. In the present work we use the sintering procedure without pressing or prolonged cycling stages, to obtain 82 wt% of the theoretical hydrogen capacity. This value is higher than those obtained using sintering with a previous pressing step [6-9, 12]. However, it is lower than that reached by cycling [13]. The time required to carry out the thermal treatment under hydrogen was the shortest in comparison with those reported in published works [6-9, 12, 13].

Figure 5 shows the first absorption isotherm at 673 K of the as-milled 2Mg-Fe sample (Fig. 5A) without sintering and a representative absorption isotherm at 673 K after sintering procedure (Fig. 5B). The XRD pattern of the as-milled sample after the PCI measurement (Fig. 4B) evidences the presence of both Mg₂FeH₆ and MgH₂ hydrides, with Mg and Fe as residual phases. As a remarkable result, the plateau obtained during the first absorption was not flat, increasing the hydrogen capacity as the pressure rises (Fig. 5A). On the other hand, when the sintering procedure was applied to the as-milled sample, an ideal plateau was observed (Fig. 5B), giving as a result a transformation in equilibrium pressure conditions. This outcome proves the importance of the sintering procedure on the hydrogen absorption/desorption behavior of the sample. It is well known that the plateau slope is essentially due to material heterogeneities which can usually be reduced by annealing [18]. In our case, the sintering procedure applied to the as-milled sample (treatment at 673 K and 6 MPa during 15 h) provides the required homogenization for the material because of Mg and Fe diffusion at high temperatures. For this system, additional undesired effects during annealing such as Mg oxidation and/or Mg volatilization might be observed but they are minimized under high hydrogen pressures. Other possible reason to observe a plateau slope is the metastable nature of the material (amorphous structures or nanocrystalline metals) [19]. Considering that mechanical alloying is a solid-state technique through which metastable materials can be produced, studies carried out by DSC and XRD analysis (not shown) proved that a thermal heating of the as-milled sample at 673 K is enough to obtain a structurally relaxed state, to crystallize potential amorphous fractions and to produce some grain growth. Then, we discard the nanocrystalline microstructure as possible explanation of the plateau slope during the as-milled 2Mg-Fe sample hydriding (Figure 5A).

A perusal of the results showed in Figures 3 and 5 indicates that during hydrogen absorption/desorption at 673 K two reactions occur at the same time. Both reactions are function of the hydrogen pressure. The hydrogen absorption/desorption process can be represented as:



In the formation process, MgH_2 and Mg_2FeH_6 practically present the same equilibrium pressures (Fig. 3A, Fig. 5B). However, during desorption we are able to identify the nature of the hydrides: a higher-pressure plateau owing to the known reaction (2) and the lower-pressure plateau owing to decomposition of Mg_2FeH_6 to Mg, Fe and hydrogen (1) (see Fig. 3B). The same behavior was observed by Bogdanović *et al.* when Mg in excess is present in a mixture ($\sim 4\text{Mg-Fe}$) [13], whereas only one plateau was obtained from a 2Mg-Fe mixture cycling (see Table I). Huot *et al.* [10] measured PCIs with two plateaus at 623 and 673 K from a dehydrided material produced by milling $2\text{MgH}_2\text{-Fe}$ under argon. We will analyze in the next section these results in the context of PCIs curves.

3.2. Thermodynamic properties of the Mg-Fe-H system

The measurements of pressure-composition isotherms for the Mg-Fe-H system were carried out in the range of 548 - 723 K (Fig. 6). Table II displays the equilibrium pressure values during the absorption/desorption and the hydrogen reversible capacity determined from the plateau widths. The calculations did not consider the formation of solid solutions, which might take place in a little extent. The plateau pressure was determined as an average value of the experimental points in the plateau region. As it was mentioned before (Fig. 3A), during hydrogen absorption it is not possible to distinguish between the formation of MgH_2 and Mg_2FeH_6 , whereas a different situation is found during desorption (Fig. 3B). In this case, relative amounts of MgH_2 and Mg_2FeH_6 can be calculated from the length of each plateau, as predicted by reactions (1) and (2) (Table II). PCI curves in Fig. 6A and 6B present similar behaviors in the temperature range of 548-673 K. After successive cycling, a flat plateau is obtained during absorption and two distinctive plateaus during desorption. That evidences the thermodynamical stability, without local heterogeneities, that the application of the sintering procedure on the as-milled sample provides to the material. Both the amount of Mg_2FeH_6 hydride and the hydrogen reversible capacity increase as the temperature rises. This phenomenon is common among

hydrides which formation involves metal atom diffusion. This mechanism is enhanced by a rise in temperature [18].

In a previous study, we observed a disproportion of the 2Mg-Fe as milled-mixture after a long thermal treatment at 673 K, caused mainly for the high vapor pressure of Mg [20]. To clarify the effect of the prolonged annealing on the properties of the Mg-Fe-H system, during the thermodynamic study the sample was intentionally subjected to an annealing at 673 K under vacuum (see §2.2). After this, isotherms at temperatures higher than 673 K (Fig. 6C) show some differences with the previous ones measured in the low temperature region (548-673 K). One consequence of this thermal treatment is that the amount of Mg_2FeH_6 decreases with the temperature from 673 K (Table II). In addition, the reversible capacity is reduced in comparison with that measured at 648 K. The results obtained evidence that the annealing under vacuum produced a change in the material composition mainly due to the high vapor pressure of Mg [18] and/or Mg oxidation. It produces sample degradation. The presence of MgO was verified from XRD performed after PCI studies by hydriding the sample at 723 K (Fig. 4C). Another effect of the annealing on the technological properties will be shown in the following.

Thermodynamic information for Mg_2FeH_6 and MgH_2 hydriding/dehydriding was determined by plotting the logarithmic dissociation pressures against the reciprocal temperature (van't Hoff plot), as shown in Figure 7. The entropy and enthalpy values per mole of hydrogen for the reactions (1) and (2) calculated from these data are given in Table III. It is important to remark the shortage of thermodynamic information reported for the Mg-Fe-H system, in particular in the low temperature range (< 673 K). In two previous works [6, 7] ΔH values have been calculated; however, it was not clearly specified the temperature range used for the calculation and/or the method employed to determine the plateau pressure. A recent investigation in the Mg-Fe-H system [13] constitutes the most complete thermodynamic studies in the authors' knowledge, since it gives the decomposition enthalpy in a wide temperature range, using different Mg-Fe compositions. In order to compare the thermodynamic parameters calculated in the present work, Table III also includes the values reported in the literature. Our values are in good agreement with those obtained by Bogdanović [13] and Konstanchuk [7], and are lower than those reported by Didisheim *et al.* [6]. The small differences might be related to the use of plateau pressures determined from PCI curves at low temperatures for the ΔH calculation.

Two additional evidences appear from the measured pressure – composition - isotherms (Figure 6). The first one, which can be seen from Fig. 7, is the slightly slope change between low (548-648 K) and high (673-723 K) temperature regions, in connection with the material

degradation. This slope modification influences the ΔH value of MgH_2 but does not affect the ΔH value of Mg_2FeH_6 . It could have been possible that Mg particles covered with Fe were less susceptible to the oxidation than those with a free surface. Therefore, the MgO detected by XRD (Fig. 4C) might have been caused by the oxidation of free surface Mg particles. The second one is the presence of hysteresis, which is common to all PCI curves obtained in this study: the change between the hydriding/dehydriding pressure is greater as the temperature increases. Although the hysteresis phenomenon is not totally understood, it has been attributed to elastic and plastic strain energies associated with large volume changes during the transformation [18]. Bogdanović *et al.* observed negligible hysteresis during PCI measurements of 2Mg-Fe-H system at 623 K, 723 K and 773 K, reaching hydrogen storage capacities of about 5 wt% [13]. Our PCI curves are similar to those obtained by Huot *et al.* [10] and by Bogdanović *et al.* for the 4Mg-Fe-H system. Then, the apparition of two plateaus (section §3.1) and the hysteresis phenomenon is due to the impossibility to bring Mg and Fe near enough to complete the Mg_2FeH_6 formation. In our work, the good Mg-Fe contacting was hampered by the big agglomerate size of the Fe particles used as starting material (Fig. 1B).

3.3. Kinetic characterization of the hydrogen reaction with the 2Mg-Fe mixture

The effect of the hydrogen pressure on the absorption kinetics was studied at 573 K and it is shown in Figure 8. A clear increase of both the absorption rate and the hydrogen storage capacity with hydrogen pressure was observed. The highest storage capacity obtained was about 3.1 wt% at 5.2 MPa, which corresponds to the formation of both MgH_2 and Mg_2FeH_6 hydrides (as verified by XRD). The maximum storage capacity at each pressure was achieved in only 800 seconds, evidencing a fast absorption rate. Although the information in the literature about the sorption kinetics for the Mg-Fe-H system is scarce, the absorption times reported for the 2Mg-Fe mixture milled involve either more than 1 h at 573 K and 1.0 MPa [16] or about 0.5 h at temperatures between 583 and 703 K [8]. Therefore, our kinetics results for the 2Mg-Fe mixture shows a better absorption rate, probably due to the special microstructural characteristics obtained as a consequence of milling, sintering and absorption /desorption cycles.

The pressure dependence on the absorption rate was determined by calculation of half reaction time, i.e. the time necessary to achieve the half reaction fraction. Figure 9 shows data obtained as a function of hydrogen pressure. It can be seen from this figure that the absorption time decreases with the increasing pressure and also becomes independent of the hydrogen pressure for values higher than 3.0 MPa.

To characterize the hydrogen sorption kinetics of the 2Mg-Fe mixture after sintering, Figure 10 shows the kinetics of hydrogen absorption and desorption at 573 K. On the basis of previous study (Fig. 8), a hydrogen pressure of 4.1 MPa was selected for the absorption reaction (Fig. 10A). The absorption rate displays two distinct regions: an initial rapid increase at short times (up to 70% conversion) and then a second region where the absorption rate continually decreases with increasing time. Previous works have shown that the overall rate reaction of hydride formation is composed of several steps, involving surface adsorption and hydrogen dissociation, migration of hydrogen atoms from the surface into the bulk, diffusion through the particle and finally nucleation and growth of the hydride phase [21]. If one of these steps is rate controlling, the kinetics of the overall process can be described by simple rate expressions. Models based on a single rate-limiting step could not fit our absorption curves. In the present work, the presence of free Fe as catalyst increases the kinetics drastically and the hydrogen dissociation step is discarded as controlling rate. The second step is not controlling when the relation surface/volume of the sample is improved. That is the general situation of milled samples and/or the materials after absorption/desorption cycles. However, mixed process involving nucleation and growth process of the hydrides and diffusion of hydrogen can be a rate-controlling step due to different crystal structure between metals and the corresponding hydrides. Then, an increase of the driving force is necessary for the creation of nucleation centers, whereas the growth of the crystallites can be controlled by the diffusion of hydrogen.

Hydrogen desorption at 573 K and 0.1 MPa for the 2Mg-Fe mixture after sintering procedure is illustrated in Fig. 10B. The desorption rate is fast and 400 seconds are enough to desorb 3 wt% of hydrogen. Our results show an improvement respect the only reported desorption curves, which involve more than 1 h at 615 K [8]. Finally, the effect of both the nature of the hydrides and the thermal history of the sample on hydrogen desorption kinetics was analyzed (Figure 11). All DSC curves show a single endothermic peak due to the decomposition of a hydride or mixed hydrides. A similar result was observed previously, when two hydrides are present [22]. When the 2Mg-Fe mixture is subjected to the first hydrogen absorption isotherm (Fig. 4B), both Mg_2FeH_6 - MgH_2 hydrides are obtained and the maximum desorption peak appears at 603 K (Fig. 11B). However, the 2Mg-Fe mixture after sintering at 673 K, cycling at high temperature (up to 723 K) and annealing at 673 K (Fig. 4C) shows the maximum desorption rate at 575 K associated with the decomposition of both Mg_2FeH_6 - MgH_2 hydrides (Fig. 11C). These results imply that chemical homogenization (see § 3.2) and microstructural modifications associated with cycling have stronger influence on the desorption kinetics than the sample degradation. It is known that upon cycling the sample suffers particle size reduction and

pulverization; both factors favoring the hydriding process. A similar desorption behavior is observed for Mg_2FeH_6 hydride obtained from the 2Mg-Fe mixture after sintering, cycling (up to 673 K) and partial desorption up to 1.0 MPa (Fig. 4A). In this sample, the intentional degradation associated with annealing under vacuum was avoided (Mg evaporation and/or MgO formation) and a reduction of the starting desorption temperature is achieved (Fig. 11C). However, it is not possible to discard the occurrence of some degradation of the material under cycling at 673 K. To clarify this, an additional sample was prepared from the 2Mg-Fe mixture performing the standard sintering procedure and cycling at low temperature (573K). The main phases obtained after absorption at 523 K under 6.0 MPa are Mg_2FeH_6 , MgH_2 and Fe (not shown). An enhancement of desorption behavior was observed: a higher desorption rate and a lower peak temperature (544 K). The above results evidence the positive role of sintering and cycling, and the relevance of avoiding further cycling at high temperature (573 K or higher). Desorption properties showed in this work do not provide evidence about a hindered effect associated with Mg_2FeH_6 presence during hydrogen desorption from the Mg_2FeH_6 - MgH_2 mixture.

4. Conclusions

Conclusions regarding the applied synthesis procedure and thermodynamic / kinetic studies carried out in this work are listed below:

1. A stoichiometric mixture 2Mg – Fe powder was processed via mechanical milling followed by a hydriding procedure (sintering) at 673 K and 6 MPa, giving as a result a mixture of Mg_2FeH_6 and MgH_2 . The relative amounts of Mg_2FeH_6 and MgH_2 were about 50 wt % and 18 wt %, respectively.
2. A clear microstructural refinement of Mg and Fe grains was obtained after 100 hours of mechanical milling. However, even after 100 hours of mechanical milling Fe particles of 30 - 40 μm can be observed. Therefore the good Mg-Fe contacting was hindered by the big agglomerate size of the Fe particles.
3. In other published works [6-9, 12], the mixture of Mg - Fe powders was pressed to cylindrical pellets in order to bring the elements close enough, so that hydriding reaction was effective. In this work, we proved that this step can be avoided, as long as a previous milling process that closes Mg and Fe particles was applied. The higher Mg_2FeH_6 yield obtained here (~ 50 wt %) in comparison with those reported in references [6-9, 12] evidenced our conclusion.

4. The time required the sintering process (15 h) was the shortest of all employed in other works [6-9, 12].
5. Through the sintering procedure, taking into account the theoretical hydrogen capacity of Mg_2FeH_6 , we obtained 82 % of the theoretical hydrogen capacity (4.5 wt %). For this reason, the reaction carried out during the hydriding involved a partial synthesis. However, the obtained hydrogen capacity is higher than those using sintering with a previous pressing step [6-9, 12], but it is lower than that reached by cycling [13].
6. We proved that the sintering process has a relevant influence upon the hydrogen absorption / desorption of the sample, since it provides the required homogenization for the material due to Mg and Fe diffusion at high temperature. All DSC analyses evidence that sintering and cycling (at temperature lower than 573 K) processes enhance the desorption kinetics. Moreover, it also contributes to the thermodynamical stability, as a flat plateau is obtained during absorption and two distinctive plateaus during desorption.
7. The amount of Mg_2FeH_6 and the hydrogen reversible capacity increase as the temperature rises. It is caused by the temperature enhanced diffusion mechanism of the metal atoms.
8. The prolonged annealing of the sample at 673 K caused a material degradation, reducing the amount of Mg_2FeH_6 and the reversible hydrogen capacity. Such degradation was originated by a change of the 2Mg – Fe stoichiometry owing to the high vapor pressure of Mg and/or Mg oxidation.
9. While the change of desorption enthalpy of MgH_2 also evidences the sample degradation caused by the prolonged annealing, desorption enthalpy of Mg_2FeH_6 was not affected. It might have been caused by the lack of susceptibility to the oxidation of Mg particles covered with Fe.
10. The thermodynamic parameters calculated in the present work are in good agreement with those reported in the literature [6, 7 and 13]. The small differences might be related to the use of plateau pressures determined from PCI curves at low temperatures.
11. The absorption rate and hydrogen storage capacity at 573 K increase as the hydrogen pressure rises, reaching the highest hydrogen capacity of 3.1 wt % at 5.2 MPa. The maximum storage capacity at each pressure is only reached in 800 seconds, which shows fast absorption kinetics.
12. Absorption time decreases as the pressure increases and becomes independent of the hydrogen pressure for values higher than 3.0 MPa.

13. Absorption/desorption rates are better than those shown in the literature, likely owing to the especial microstructural characteristics of the material.

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CAPTIONS

Figure 1: Secondary electrons micrographs (SEM) showing the starting materials used for the 2Mg-Fe mixture: (A) Mg powder and (B) Fe chips.

Figure 2: X-ray diffraction pattern of the 2Mg-Fe mixture after 100 h of milling. Backscattered electron micrographs of the 2Mg-Fe mixture after milling for (A) 2h and (B) 100 h.

Figure 3: (A) First hydrogen absorption kinetics at 673 K and 6 MPa of the 2Mg-Fe milled 100 h. (B) Desorption isotherm at 673 K of the 2Mg-Fe mixture after hydriding according to (A).

Figure 4: X-ray diffraction pattern of the 2Mg-Fe as-milled mixture after: (A) Partial desorption isotherm up to 1 MPa at 673 K (see arrow in Fig. 3B); (B) First hydrogen absorption isotherm at 673 K without previous sintering procedure; (C) Absorption isotherm at 723 K, after degradation by annealing.

Figure 5: (A) First hydrogen absorption isotherm at 673 K of the 2Mg-Fe as-milled mixture. (B) Typical absorption isotherm at 673 K of the 2Mg-Fe as-milled mixture after sintering.

Figure 6: Pressure composition isotherms for the 2Mg-Fe-H system at different temperatures. (A) 548K and 573 K; (B) 598 K to 648 K; (C) 673 K to 723 K (sample degraded).

Figure 7: Van 't Hoff plot of 2Mg-Fe-H system (information from Fig. 6).

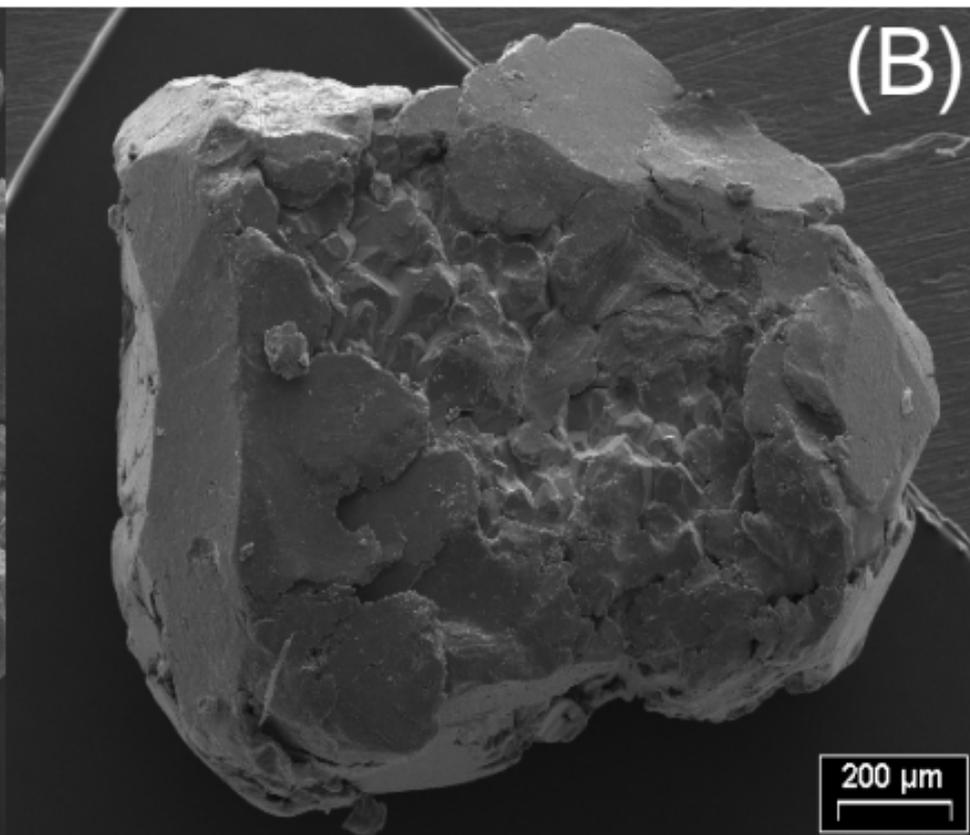
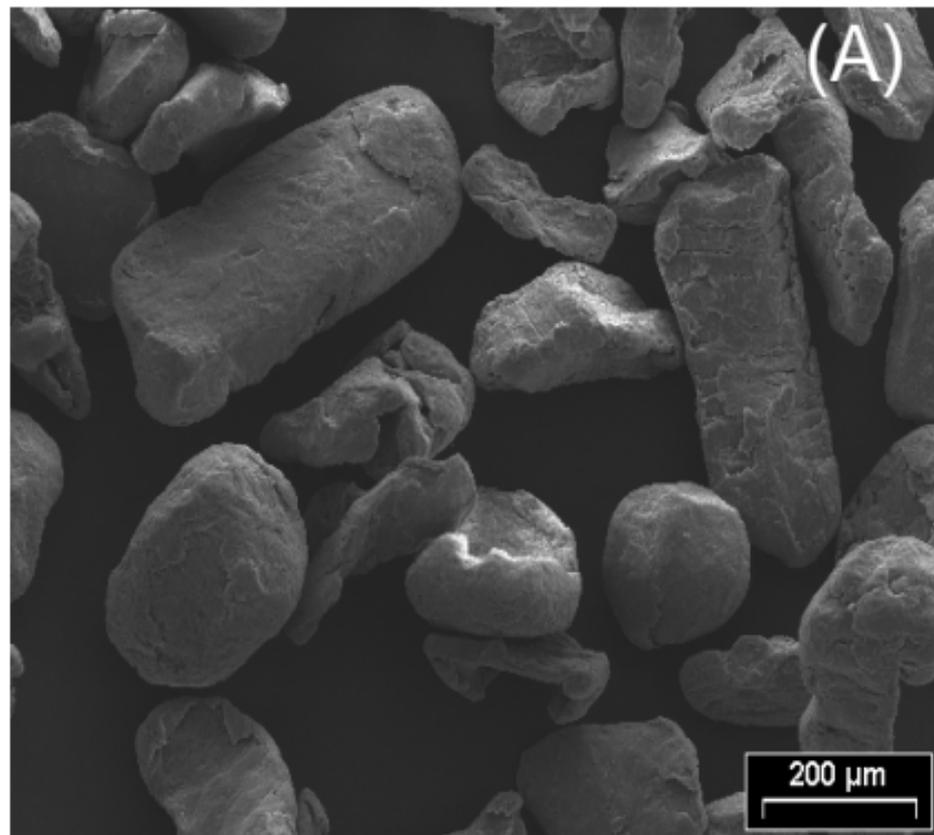
Figure 8: Effect of the hydrogen pressure on the hydrogen absorption rate at 573 K for the 2Mg-Fe mixture after sintering procedure.

Figure 9: Dependence of the half reaction time versus hydrogen pressure at 573 K.

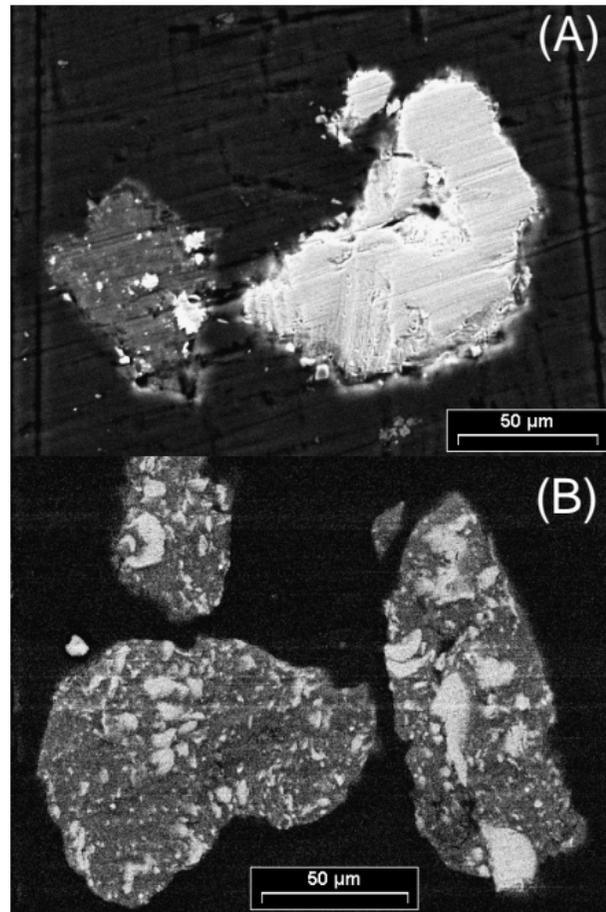
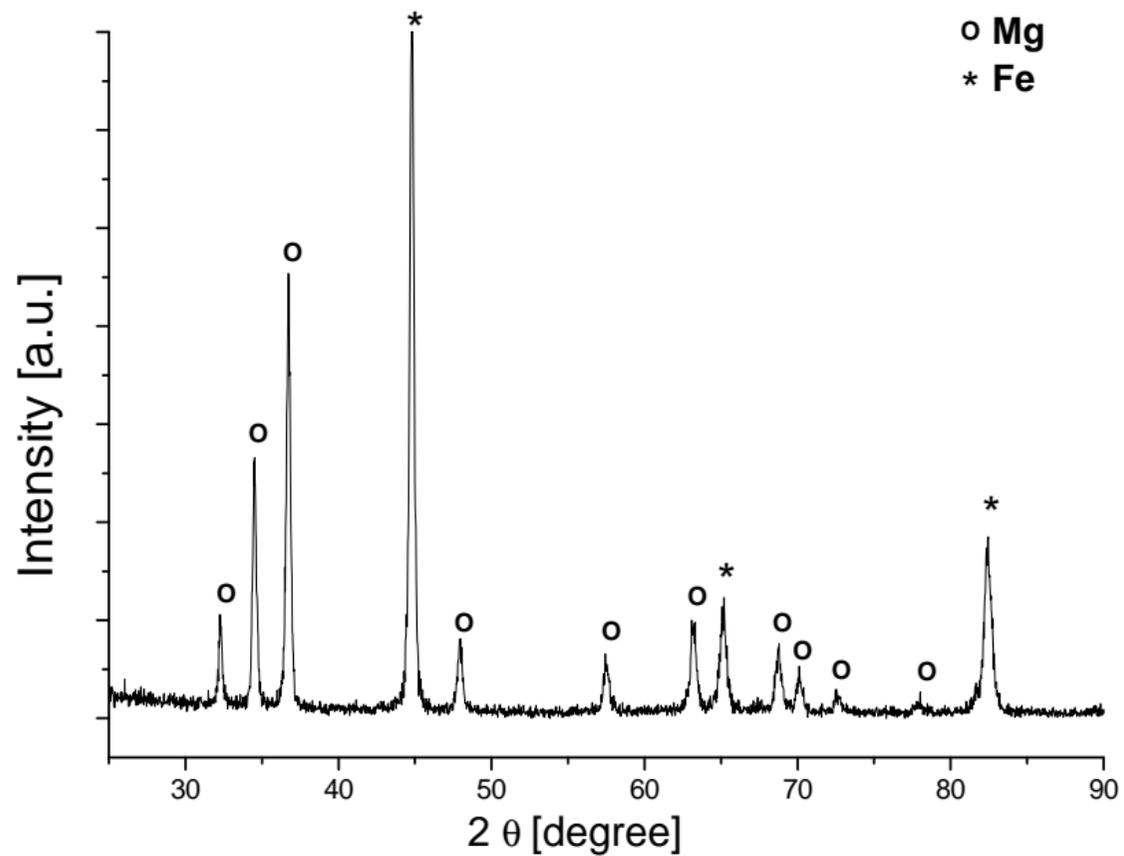
Figure 10: Hydrogen (A) absorption and (B) desorption at 573 K for the 2Mg-Fe mixture after sintering procedure. Initial hydrogen pressure during absorption $P_i=4.1$ MPa. Desorption pressure $P_d= 0.1$ MPa.

Figure 11: Hydrogen desorption from the 2Mg-Fe mixture after: A) Partial desorption up to 1 MPa at 673 K; B) First hydrogen absorption isotherm at 673 K without previous sintering procedure; C) Absorption isotherm at 723 K, after degradation by annealing; D) Absorption at 523 K under 6.0 MPa.

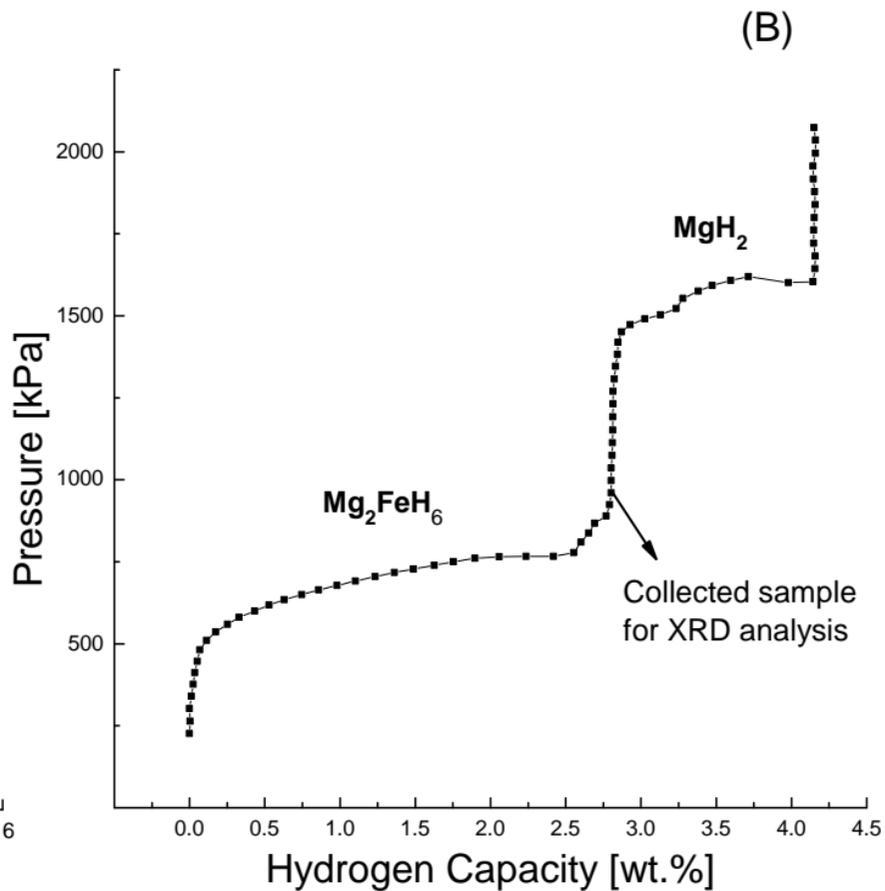
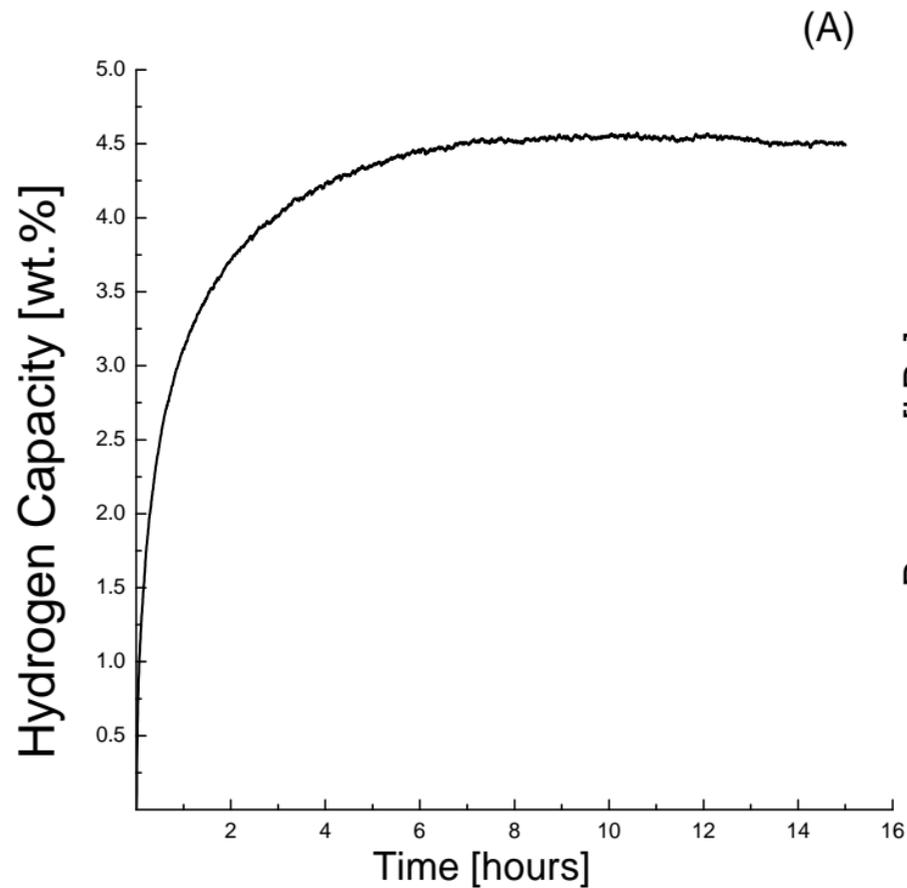
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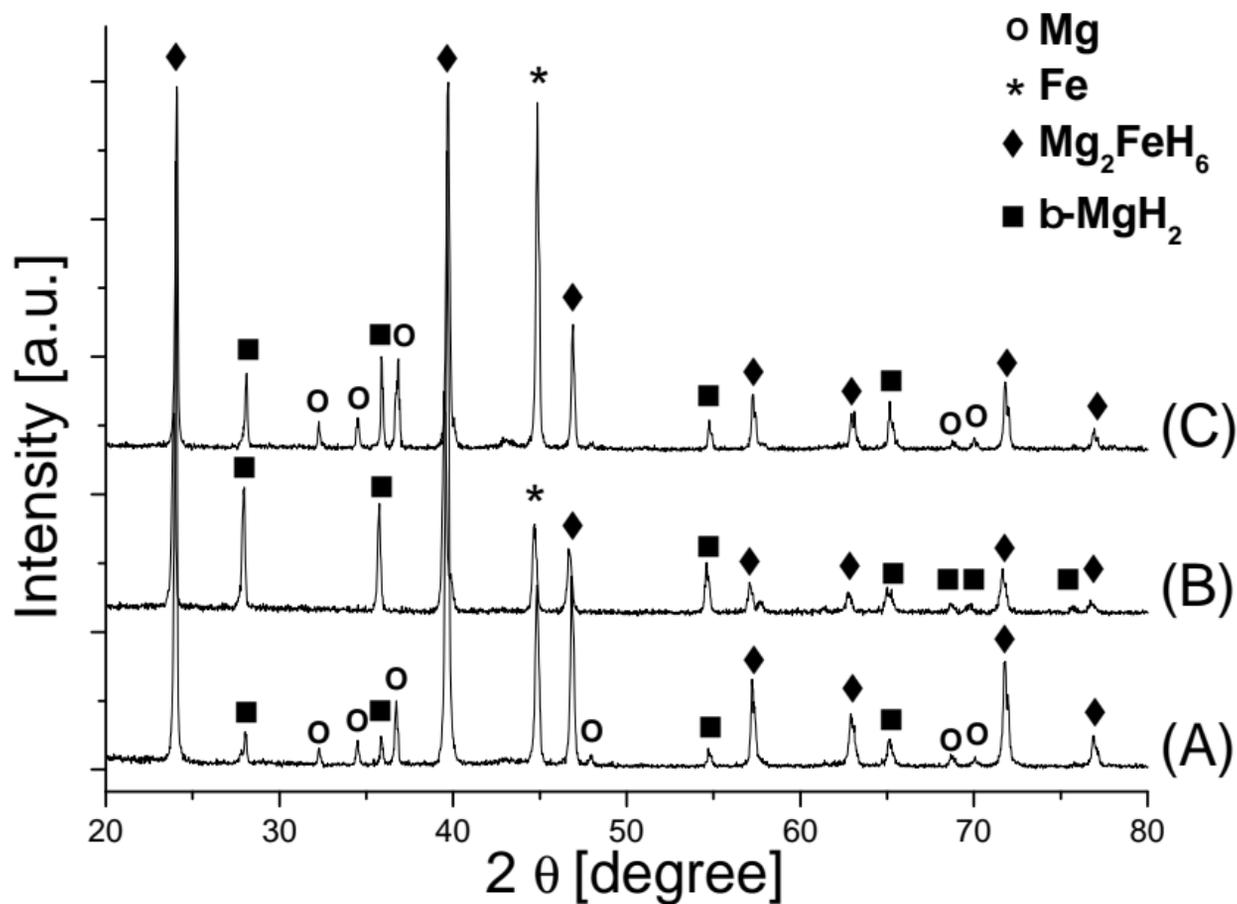
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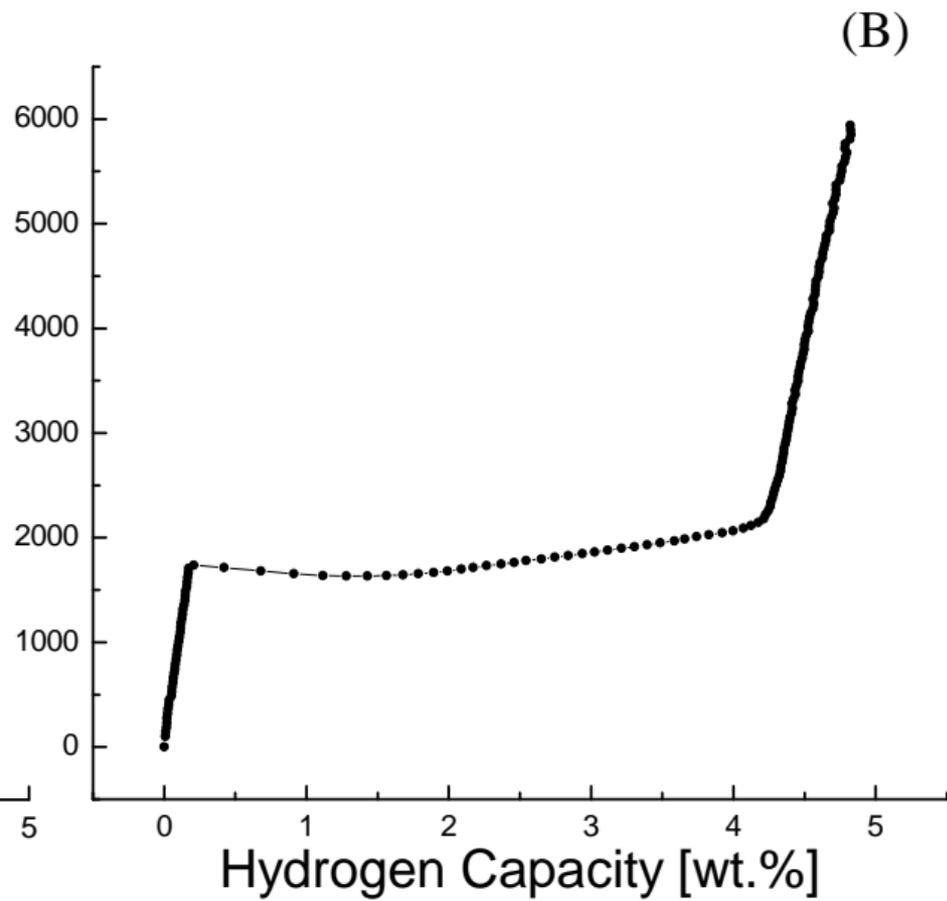
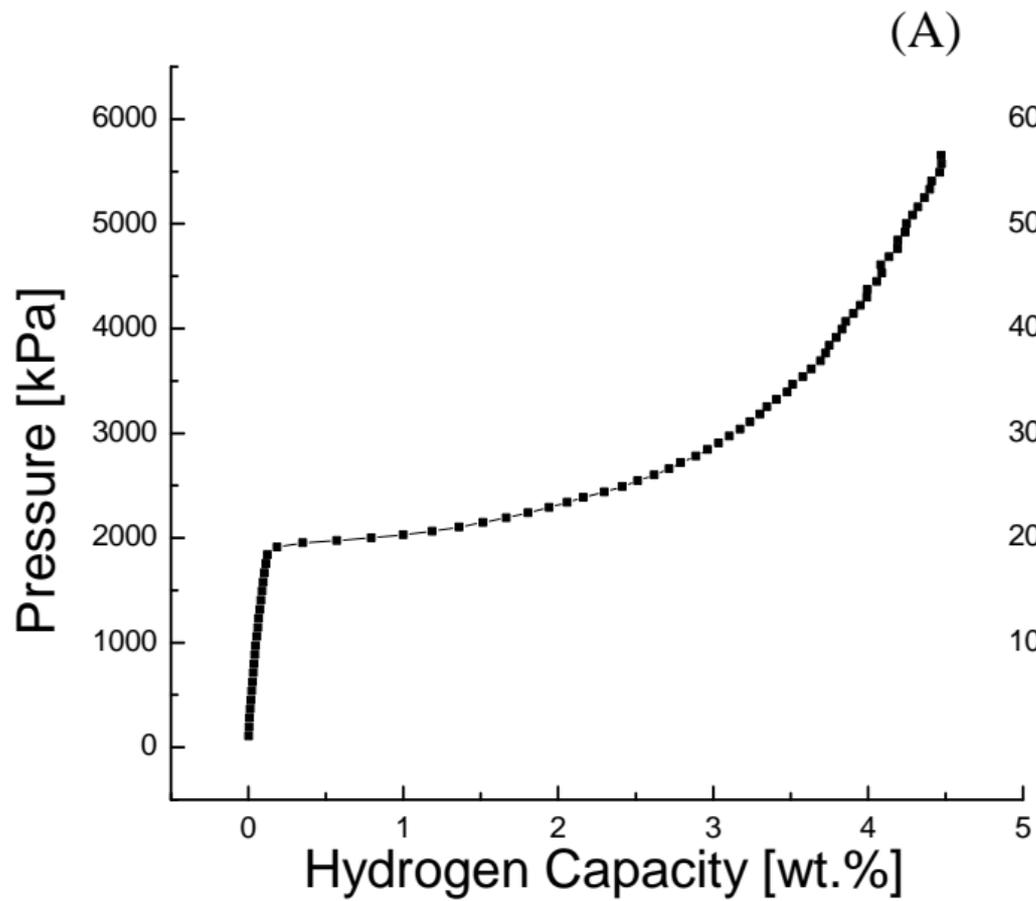
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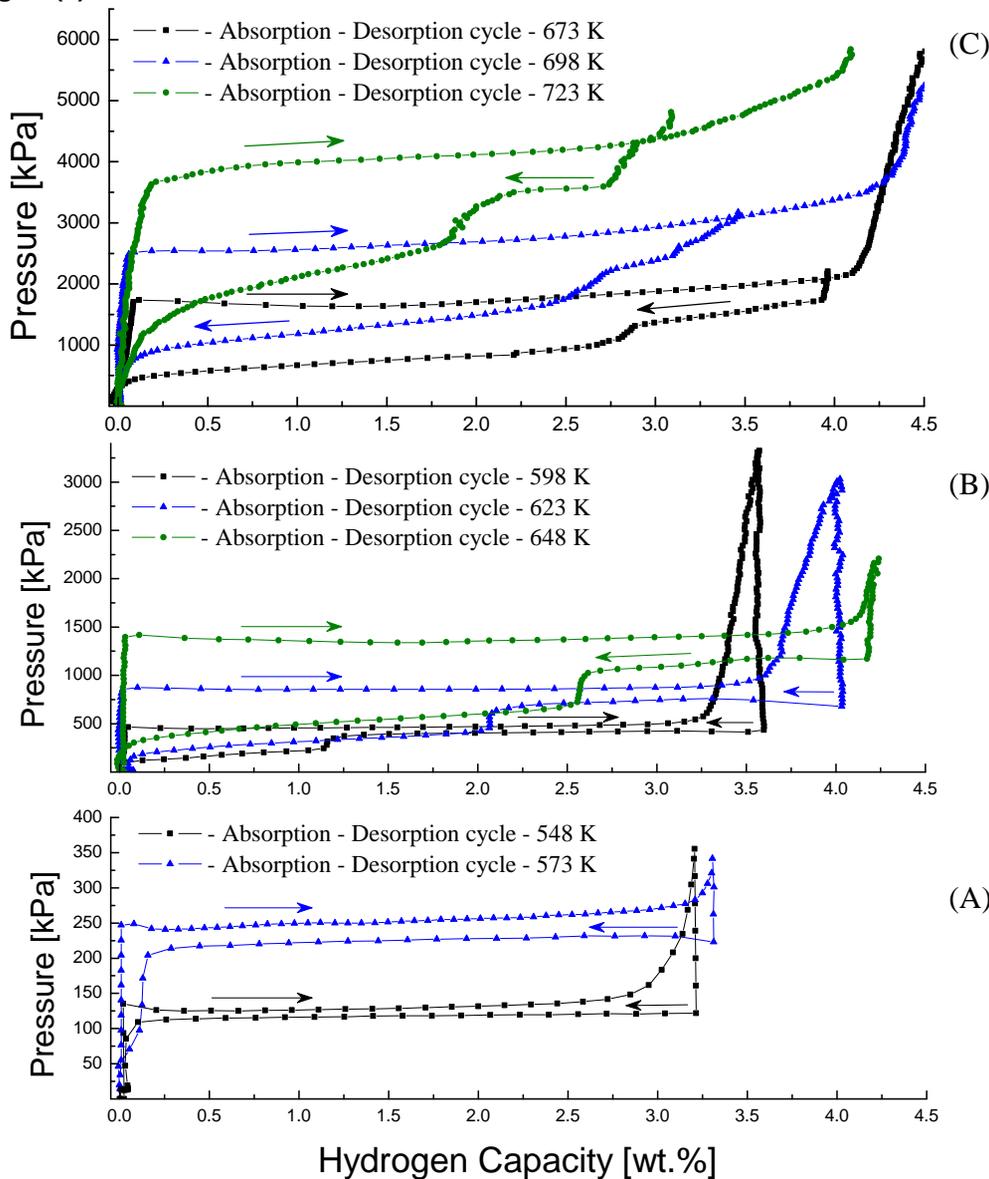
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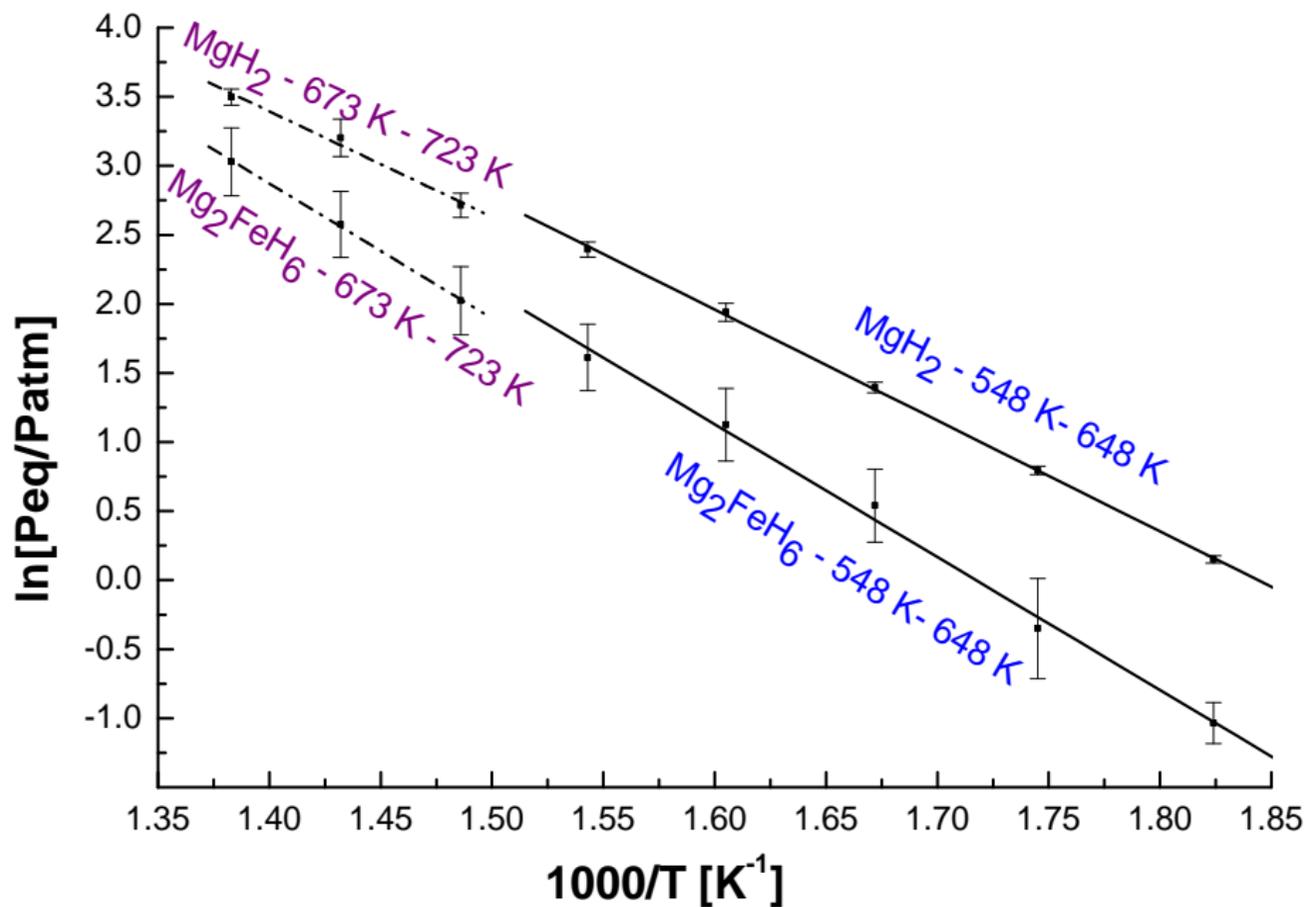
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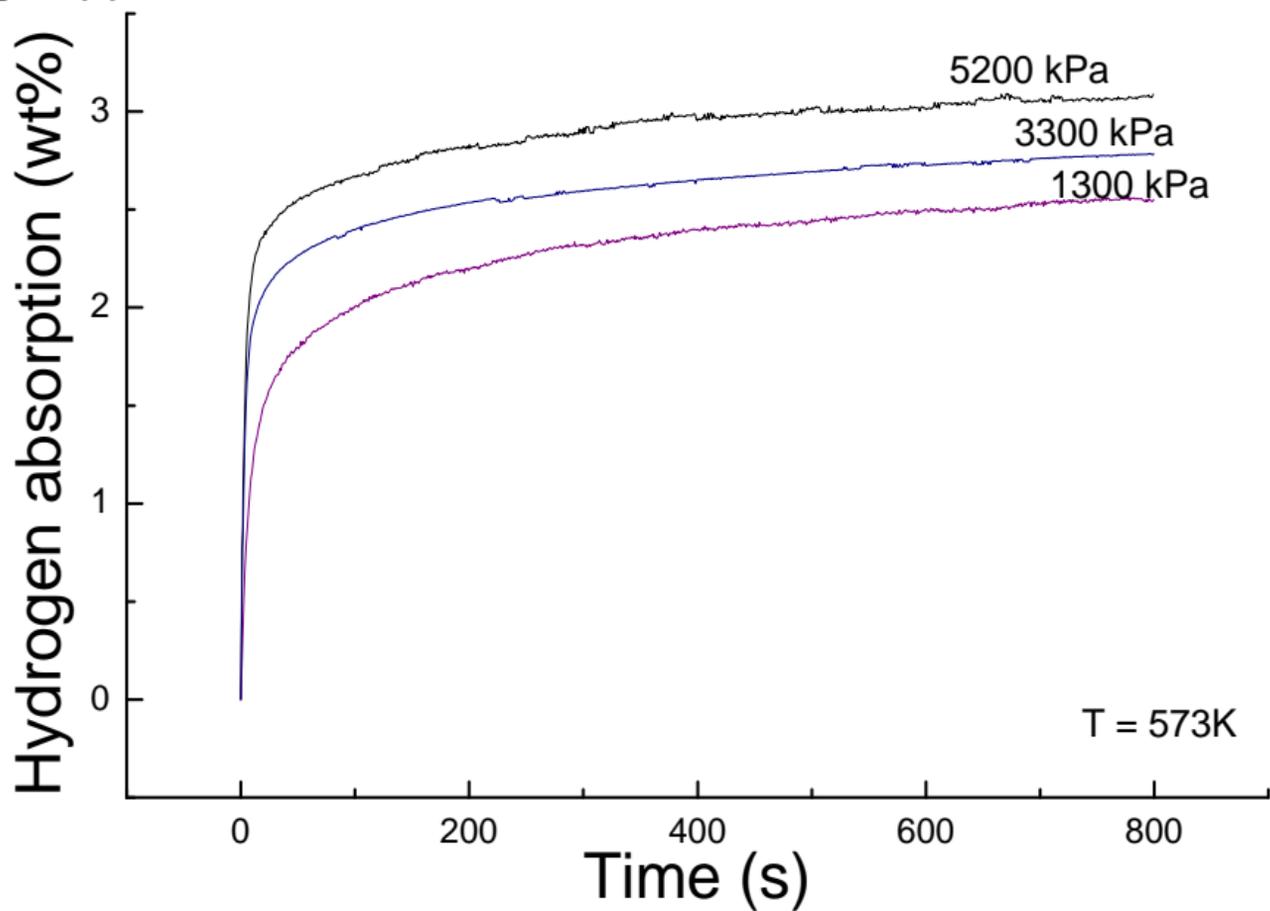
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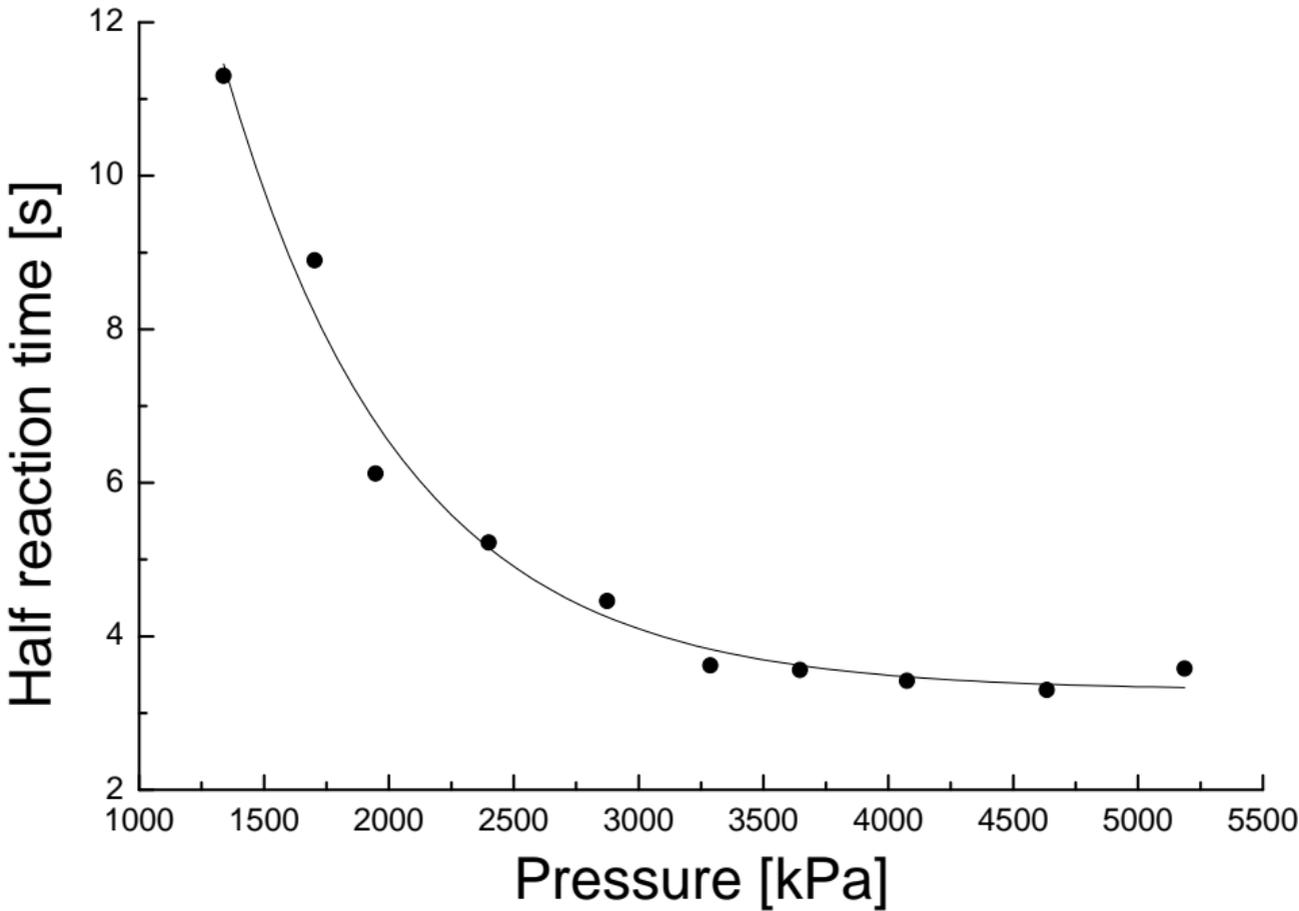
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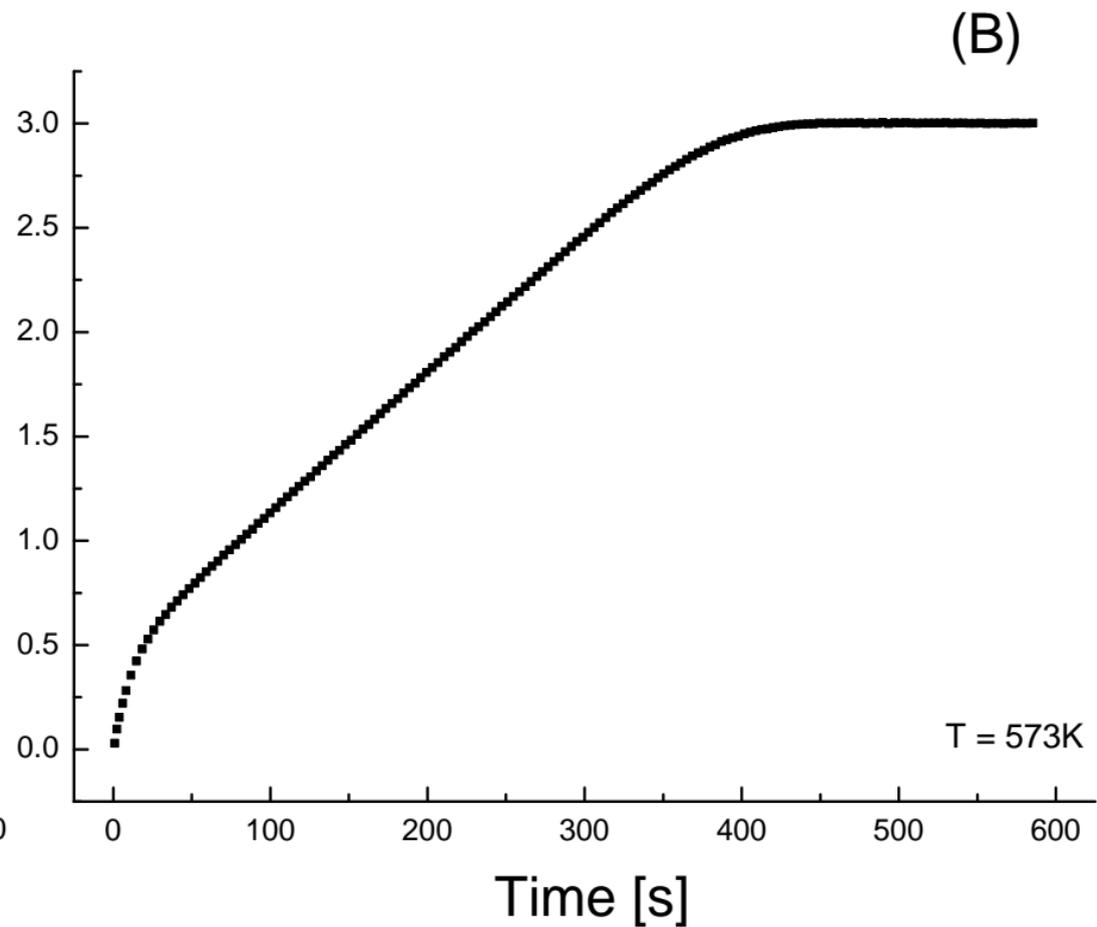
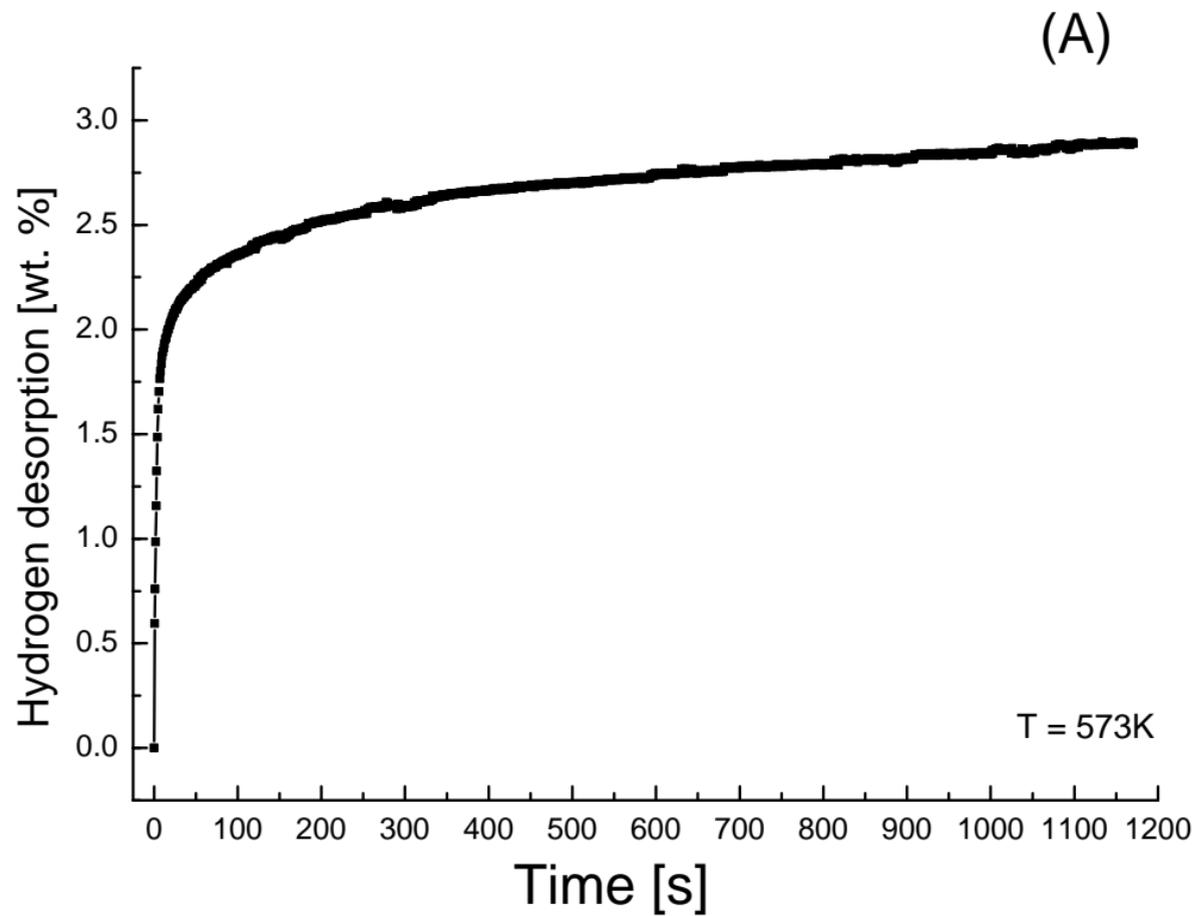
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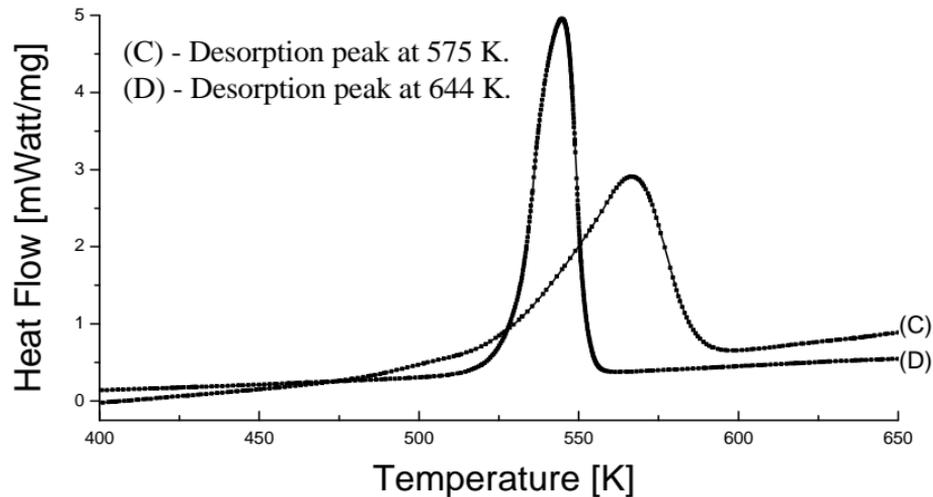
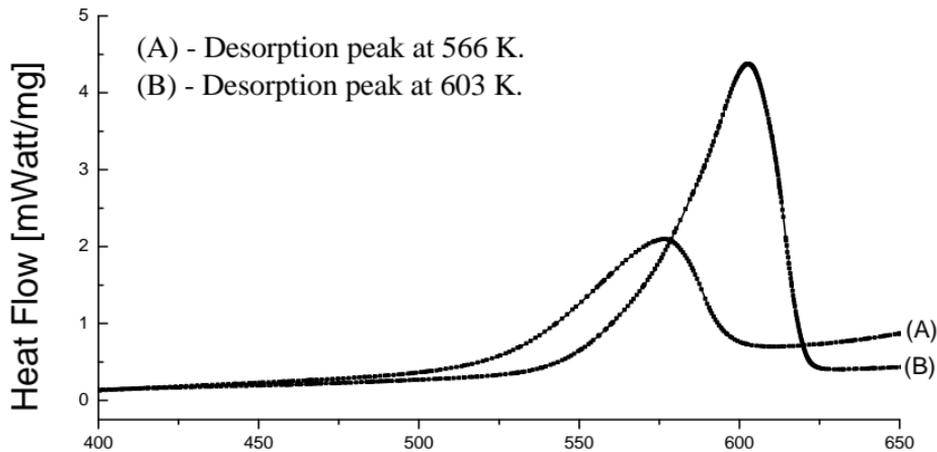


Table I: Synthesis procedure, experimental conditions and hydrogen storage capacity obtained during Mg_2FeH_6 formation

| Synthesis | Starting materials | Pressing, MM and/or cycling | Experimental conditions ⁽¹⁾ | Hydrogen content | Ref. |
|-----------|--------------------------|---|--|--|-----------|
| Sintering | 2Mg-Fe | Pressing | 723-793 K, 2.0-12 MPa, 2-10 days | ~2.7 wt% | [6] |
| | ~6Mg-Fe | MM (Ar) | 583-703 K, 0.7-4 MPa | 3.6 wt% ⁽²⁾ | [7] |
| | 2Mg-Fe | pressing | 723-773 K, 0.7-4.0 MPa, 7-10 days | high | [8] |
| | 2Mg-Fe | MM (Ar or H ₂) and pressing | 623 K, 5.0 MPa, 1 day | ~1.2 wt% (Ar) 3.6 wt% (H ₂) | [9] |
| | 2Mg-Fe | cycling | 723-820 K, 8.2-9.5 MPa, 223 cycles | ~5.0 wt% | [13] |
| | 2MgH ₂ -Fe | cycling | 673-793 K, 4.0-4.4 MPa, 50 cycles | 4.6 wt% | [13] |
| | 2Mg-Fe | MM (Ar) and pressing | 723 K, 5.0 MPa, 2-5 days | 3.4 wt% | [12] |
| | 2Mg-Fe | MM (Ar) | 673 K, 6.0 MPa, 15 h | 4.5 wt% ⁽²⁾ | This work |
| MM | 2MgH ₂ -Fe | MM (Ar) | r.t, 0.1 MPa, 60 h | 3.1 wt% | [10] |
| | 2Mg-Fe | MM (H ₂) | r.t, 0.5 MPa, 60 h | 1.6 wt% | [11] |
| | 2Mg-Fe | MM (H ₂) | r.t, 1.0 MPa, 20 h | 3.4 wt% | [12] |
| | 2MgH ₂ -Fe | MM (H ₂) | r.t, 0.5 MPa, 100 h | 0.9 wt% | [14] |
| | 2Mg-Fe | MM (H ₂) | r.t, 0.75 MPa, 270 h | 1.9 wt% | [15] |
| | 2MgH ₂ -0.5Fe | MM (H ₂) | r.t, 0.7 MPa, 80 h | 4.9 wt% | [16] |

⁽¹⁾ Experimental conditions are given in correlation with the synthesis procedure

⁽²⁾ Hydrogen content includes the presence of MgH_2 .

Table II: Equilibrium pressures and relative amount of MgH_2 and Mg_2FeH_6 hydrides as a function of temperature, determined from Figure 6.

| Temperature (K) | Absorption | | Desorption | | | |
|-----------------|--|------------------------|-----------------------|------------------------|---------------------------|------------------------|
| | MgH_2 - Mg_2FeH_6 | | MgH_2 | | Mg_2FeH_6 | |
| | P_{eq} [kPa] | Hydrogen content [wt%] | P_{eq} [kPa] | Hydrogen content [wt%] | P_{eq} [kPa] | Hydrogen content [wt%] |
| 548 | 135 | 3.0 | 120 | 3.1 | - | - |
| 573 | 260 | 3.3 | 220 | 3.2 | 70 | 0.14 |
| 598 | 470 | 3.2 | 400 | 2.3 | 170 | 1.3 |
| 623 | 870 | 3.5 | 700 | 2.0 | 310 | 2.0 |
| 648 | 1340 | 4.0 | 1110 | 1.6 | 510 | 2.6 |
| 673 | 1830 | 4.0 | 1530 | 1.0 | 780 | 2.9 |
| 698 | 2970 | 4.3 | 2490 | 0.8 | 1330 | 2.6 |

Table III: Enthalpy and entropy values for the formation and decomposition of MgH_2 and Mg_2FeH_6 hydrides calculated from the van't Hoff plot (Fig.7).

| Absorption | MgH ₂ and Mg ₂ FeH ₆ | | | |
|-------------------------|---|--|--|--|
| | $\Delta\text{H} [\text{kJ}\cdot\text{mol}^{-1} \text{H}_2]$ | | $\Delta\text{S} [\text{J} \cdot \text{mol}^{-1} \text{H}_2 \text{K}^{-1}]$ | |
| This work (548 - 723 K) | - 66 ± 2 | | - 124 ± 3 | |
| Ref. [6] (698-723 K) | -55 ± 3 | | - | |
| Desorption | MgH ₂ | | Mg ₂ FeH ₆ | |
| | $\Delta\text{H} [\text{kJ}\cdot\text{mol}^{-1} \text{H}_2]$ | $\Delta\text{S} [\text{J} \cdot \text{mol}^{-1} \text{H}_2 \text{K}^{-1}]$ | $\Delta\text{H} [\text{kJ}\cdot\text{mol}^{-1} \text{H}_2]$ | $\Delta\text{S} [\text{J} \cdot \text{mol}^{-1} \text{H}_2 \text{K}^{-1}]$ |
| This work (548 - 648 K) | - 67 ± 2 | - 123 ± 3 | - 80 ± 7 | -137 ± 13 |
| This work (673 - 723 K) | - 62 ± 8 | - 116 ± 12 | - 81 ± 28 | -137 ± 13 |
| Ref. [6] (648-723 K) | - | - | - 98 ± 3 | - |
| Ref. [7] (623-698 K) | - 77 ± 4 | - 138 ± 3 | - 86 ± 6 | - 147 ± 9 |
| Ref. [13] (623-798 K) | - | - | - 77 | - |