

Hydrogen Absorption and Desorption Performance of Magnesium-Aluminium Alloys Produced by Powder Metallurgy

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Summary: The main scope of this study is investigating the hydrogen storage and desorption performance of Mg: Al (90:10), Mg₁₇Al₁₂ and Mg₂Al₃ alloys using a volumetric method. In the experiments, hydrogen pressure introduced into a reference volume was at approximately 20 Bar. Mg-Al alloys were prepared by a powder metallurgy technique. Pressing pressure levels of alloys were altered as 200, 400 and 600 MPa. Upon XRD patterns, after the pressing and sintering, β -Mg₂Al₃ and Mg:Al(90:10) phases decomposed into γ -Mg₁₇Al₁₂, Mg and Al compositions. γ -Mg₁₇Al₁₂ was the main phase in the hydrogen absorption/desorption process. The highest absorption of hydrogen was observed in the Mg:Al (90:10) alloys. The hydrogen desorption performance of the alloys decreased with the increase of absorption performance. Therefore the lowest desorption was observed in the Mg:Al (90:10) alloys.

Keywords: Metal alloys; Hydrogen storage and Desorption; powder metallurgy

Introduction

Modern industrialised societies, which have had their economic growth based on the utilisation of energy locked in fossil fuels, can no longer ignore the effects of fossil fuels such as global warming, climate changes and natural disasters. The demand for energy continues to rapidly rise due to the continuing increase of the world population and the growing demand from developing countries to improve their living standards. The solution to this global energy problem need clean energy technologies. The development of efficient methods for hydrogen storage is a major issue that must be overcome in order to enable the use of hydrogen as an alternative energy carrier. The development of high capacity hydrogen storage materials that can be recharged under moderate conditions is a key barrier to the realisation of a hydrogen economy. Several studies report the development of hydrogen storage materials such as metal hydrides, carbon- based materials, chemical hydrides, boron compounds, etc. [1].

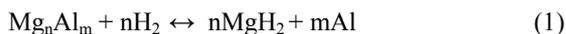
Among the known alloys with potential use in the hydrogen storage, Mg and Mg-based metallic hydrides are considered to be the most promising materials for hydrogen storage due to their high hydrogen capacity and low cost. Unfortunately, the practical applications are limited due to the poor absorption/desorption kinetics and high thermodynamic stability of these kinds of metal

hydrides [2]. Therefore, various attempts have been made to reduce the thermodynamic stability, including alloying with transition or rare earth metals, adding fine oxide particles, adding halides, producing hydrides with a nano-crystalline structure, electrochemical hydriding and others [3].

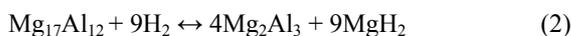
To obtain the lightweight hydrogen storage alloy, element Al has been studied regarding its ability to interact with Mg as hydrogen storage material due to its low density and perfect thermal conductivity. Bouaricha *et al.* [4] reported the hydriding behaviour of Mg–Al and leached Mg–Al compounds prepared by high-energy ball milling. The measured hydrogen capacity of the milled material decreases with the Al content, from H/M=1.74 for pure un-milled Mg, to 1.38 for Mg:Al (90:10), and then to 1.05 for Mg:Al (75:25). Zaluska *et al.* [5] examined, with examples from a wide range of hydrides, the direct impact of the nano-scale structure, subsequent improvements in kinetics through nanoscale solid state catalysis, the special properties of nanocomposites, and the role played by nano-scale reactions. Their example of a functional nano-composite was that Mg–Al. Magnesium brings to the system high hydrogen capacity which, even after including the presence of Al, can reach 3.5–4.5wt. %. Aluminium provides improved heat-transfer properties and modifies the hydrogenation thermodynamics in such a way that the system can

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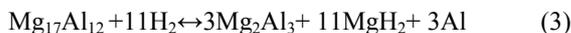
operate at lower temperatures. Andreasen *et al.* [6] studied the interaction of hydrogen with an Mg–Al alloy pre-exposed to air with in situ time resolved X-ray powder diffraction. The results showed that the addition of Al improved the resistance to oxygen contamination. Wang *et al.* [7] synthesised a composite containing Mg₁₇Al₁₂ alloy and MgH₂ by ball milling. In comparison with the hydrogenation of Mg₁₇Al₁₂ alloy and MgH₂, the synergistic effect of ball-milled MgH₂ and Mg₁₇Al₁₂ alloy on the hydrogen hydriding/dehydriding behaviour of the composite was discussed. Milanese *et al.* [8] have prepared nano-crystalline binary mixtures of Mg and nine different metals (Al, Cu, Fe, Mo, Mn, Sn, Ti, Zn and Zr) using mechanical alloying; their sorption capacities have been compared in order to study the effect of these additives as catalysing/destabilising agents for Mg hydrogenation/ dehydrogenation. They found total H₂ intake and sorption efficiencies for compositions Mg 70% + Al 30%, Mg 55% +Al 45%, Mg 37% +Al 63%. For Mg–Al systems the general reaction scheme is:



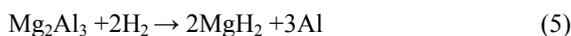
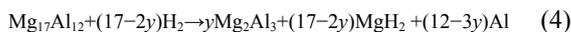
For 70% Mg 30% Al alloy;



For 55% Mg 45% Al and 37% Mg 63% Al alloys;



These reactions are also expressed as follows for Mg₁₇Al₁₂ [4, 9]. Initially, only Mg₁₇Al₁₂ is decomposed to Mg₂Al₃ and formed the MgH₂, and then Mg₂Al₃ is reacted for the resulting MgH₂;



Crivello *et al.* [10] reported encouraging results for Mg–Al system with Nb₂O₅ additive catalyst. Three nominal compositions [(Mg_xAl_{100-x})-99 + (Nb₂O₅) - 1 mol.%], X = 100 (Mg), X = 39 (β-Mg₂Al₃) and X = 70 (Mg + γ-Mg₁₇Al₁₂) have been investigated for their hydrogen equilibrium pressure of absorption and desorption reactions, from 250°C to 400°C. Glage *et al.* [11] presented a Powder Metallurgy (PM) route for the production of a hydrogen storage MgH₂–Al composite material. Pure

aluminium specimens were sintered with two different sets of sintering parameters in order to investigate their effect on the properties of the matrix material after the sintering process. Next, a bulk composite consisting of MgH₂ and 20 wt.% Al was produced in order to evaluate the resistance to decrepitation. Tanniru *et al.* [12] evaluated the hydrogenation characteristics of an Mg–8at% Al alloy powder synthesised using the electro deposition technique to investigate the effect of Al addition on the stability of magnesium hydride. The characterization of the hydrogenation behaviour within the 180°C–280°C temperature range and the subsequent micro structural analysis elucidated that the amount of Al present in the hydride decreased with the increasing temperature. Hydrogenation properties and mechanical stability of pellets made starting from compressed ball-milled MgH₂ powders mixed with catalysts (Nb₂O₅ and graphite) and a binding agent (aluminium powder) have been investigated by Khandelwal *et al.* [13]. The best cycling behaviour and mechanical strength stability have been observed for pellets of catalysed MgH₂ powders added with 5 wt% aluminium annealed in a vacuum at 450°C before starting the a/d cycles. Kalisvaart *et al.* [14] focused on the hydrogen sorption properties of 1.5mm thick Mg-based films with Al, Fe and Ti as alloying elements. The binary alloys are used to establish a baseline case for the ternary Mg–Al–Ti, Mg–Fe–Ti and Mg–Al–Fe compositions. They show that the ternary alloys in particular display remarkable sorption behaviour at 200 °C the films are capable of absorbing 4–6 wt% hydrogen in seconds, and desorbing in minutes.

The main scope of this study is to investigate the H₂ absorption and desorption performance of Mg:Al (90:10), Mg₁₇Al₁₂ and Mg₂Al₃ alloys, produced in different press and sintering conditions, using a volumetric method.

Results

Physical Characterization of Materials

In order to define the formation of phases in the alloys, a Rigaku XRD diffractometer was used. The X-ray analysis was operated at 30 kV, 30 mA with Cu Kα radiation. XRD results confirmed the presence of crystalline phases, Mg, Al, Mg₂Al₃, Mg₁₇Al₁₂, MgAl₂O₄, see Figs. 1-3.

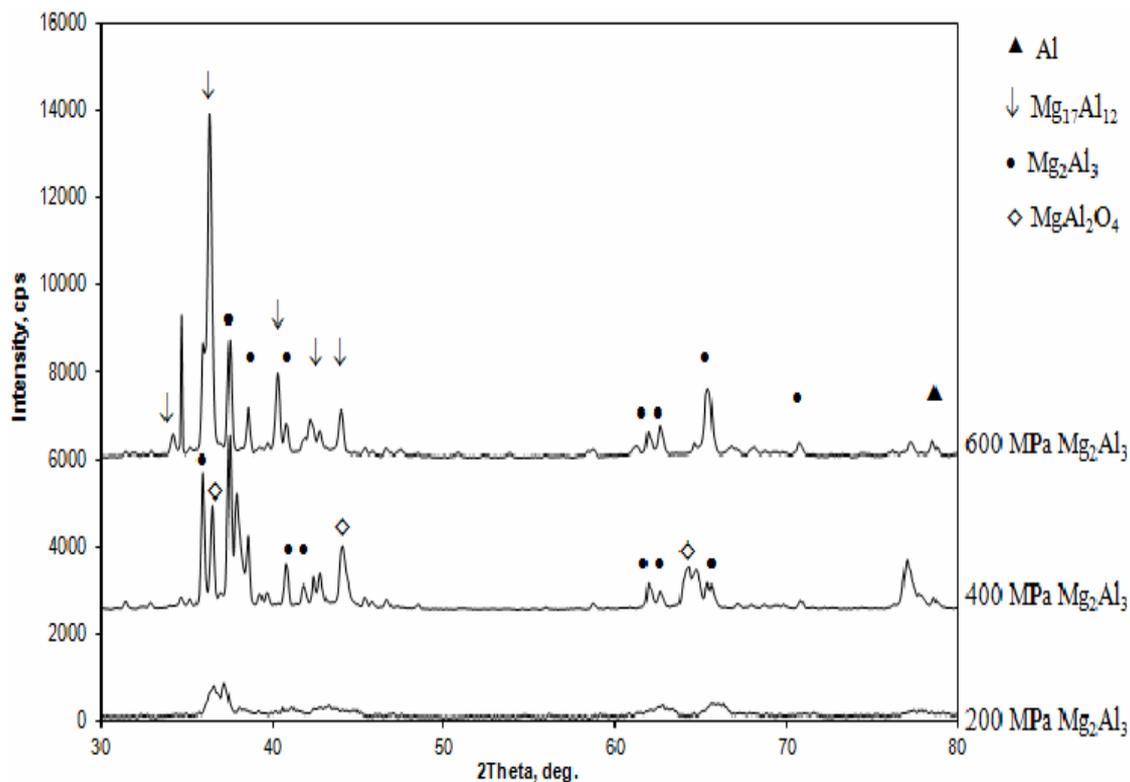


Fig. 1: XRD patterns of Mg_2Al_3 alloys.

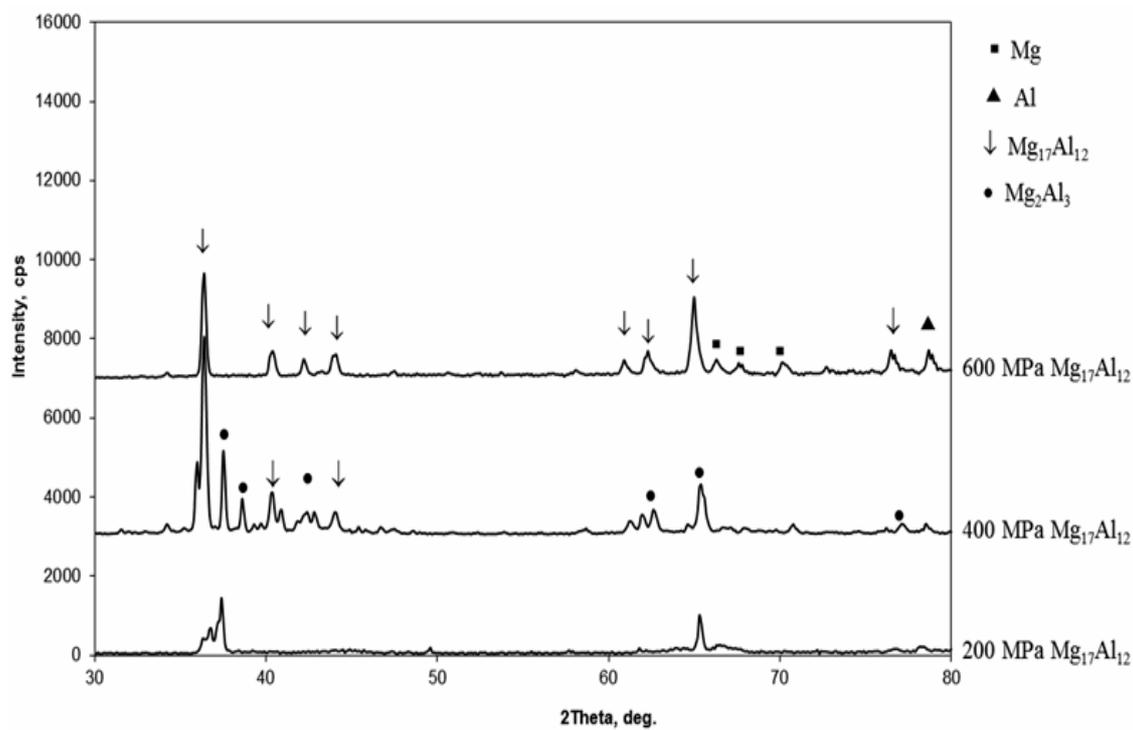


Fig. 2: XRD patterns of $Mg_{17}Al_{12}$ alloys.

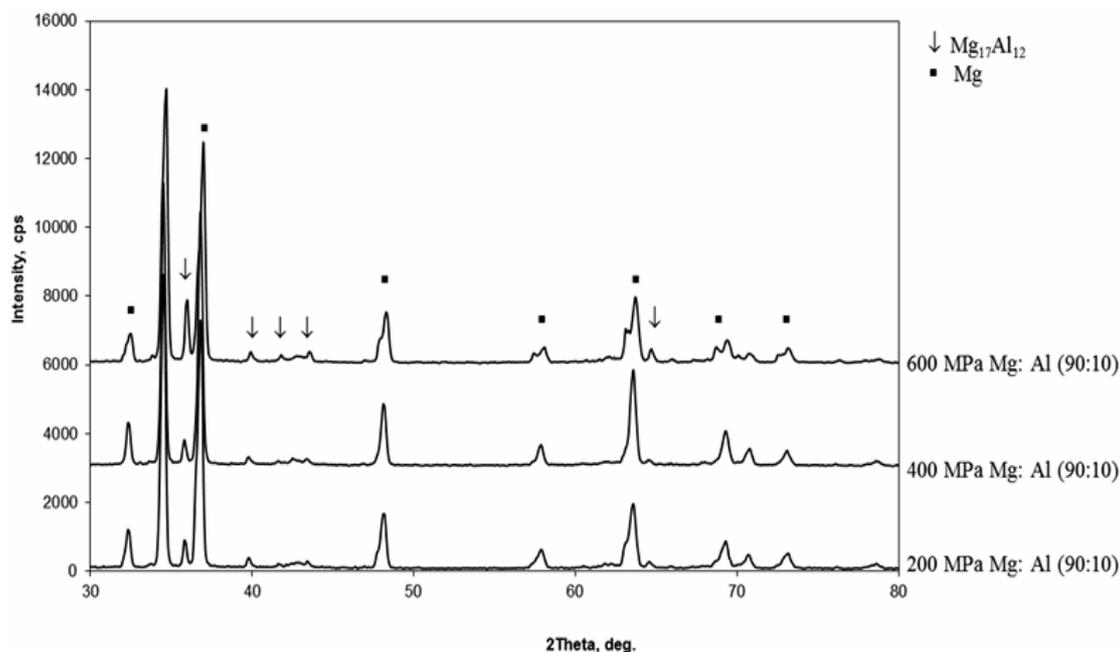


Fig. 3: XRD patterns of Mg:Al (90:10) alloys.

Hydrogen Absorption and Desorption

The hydrogen storage performance of the Mg-Al alloys is mainly denoted by the hydrogen absorption and desorption capacity.

- The effect of the alloy types and pressing conditions for hydrogen absorption and desorption are presented in Fig. 4 and Fig. 5, respectively.
- It was obtained from the XRD patterns of $Mg_{17}Al_{12}$ alloy that the phase of 600MPa $Mg_{17}Al_{12}$ was a pure phase. Therefore, the hydrogen absorption ratio of this alloy was the highest (Fig. 4).
- The existence of Mg_2Al_3 decreased the hydrogen absorption. It is shown in Fig. 4 that absorbed H_2 weight of 200 and 400MPa $Mg_{17}Al_{12}$ alloys were lower than 600MPa $Mg_{17}Al_{12}$, because of existing of Mg_2Al_3 (XRD patterns of $Mg_{17}Al_{12}$ presented in Fig. 2).
- The porosities of 600MPa $Mg_{17}Al_{12}$ and 400MPa Mg:Al(90:10) were the same value of 76.4. Therefore, as seen in Fig. 4 and Fig. 5, their hydrogen absorption and desorption characteristics were the same.
- According to the Mg-Al binary phase diagram, higher Mg concentration led to the formation of 2-phases compound; composed Mg- phase and γ - $Mg_{17}Al_{12}$ phases. According to the XRD data, it can be clearly seen that Mg rich Mg:Al (90:10) phase was transformed into the γ - $Mg_{17}Al_{12}$ and Mg phases. Comparing all alloys with XRD patterns, the maximum amount of the γ - $Mg_{17}Al_{12}$ phase and the maximum hydrogen absorption were managed with Mg:Al (90:10) alloys.
- From the XRD results, Al in the alloys of Mg_2Al_3 and $Mg_{17}Al_{12}$ dissolved under pressure and the weight of Al increased in the phases with increasing pressure (Fig. 1 and Fig. 2). The hydrogen desorption performance of the alloys decreased with the increasing Al content (Fig. 5). Dai *et al.* [15] studied the Al, Ti, Mn, and Ni doped MgH_2 systems and found that adding Al marginally increases the dehydrogenation energy.
- The formation of $MgAl_2O_4$ was observed in Mg_2Al_3 phase from XRD patterns of Fig. 1. In this phase Al formation was restricted because of the contribution of oxidized species to slow the kinetics of Al dissolution. Therefore dehydrogenation efficiency of 400MPa Mg_2Al_3 was better than 200MPa Mg_2Al_3 due to the deficiency of Al.
- The lowest absorption and the highest desorption values of hydrogen were received from Mg_2Al_3 and $Mg_{17}Al_{12}$ alloys which were pressed at 200MPa. These alloys had the same pure Mg_2Al_3 phase (Fig. 1 and 2).
- It can be clearly seen from Table-1 and Fig. 5 that the Mg_2Al_3 , $Mg_{17}Al_{12}$ and Mg:Al (90:10) alloys pressed at 200 MPa had larger porosity

- 2- The sample was charged into the sample container and the system was closed. A vacuum pump was operated continuously for 15 minutes.
- 3- The experimental apparatus was isolated from the vacuum system by closing the isolation valve. In addition, the sample container was isolated using the sample isolation valve.
- 4- H₂ gas was introduced into the reference volume and the pressure was recorded. Approximately 20 bar was the supply pressure of the reference volume.
- 5- The sample isolation valve was opened in order to start absorption. The system pressure change was recorded.
- 6- The sample container was heated to 80°C (2°C/minute) gradually and maintained at this temperature for 260 minutes.
- 7- After 5 hours, the sample container was cooled to room temperature to lock H₂ in the crystal lattice of the alloys. The sample isolation valve was closed again and the needle valve, which was inserted between the sample container and burette, was opened to measure the H₂ volume.
- 8- The sample container was discharged and isolated once again, and the procedure was returned to 2. Next, procedures 2-7 were repeated and the H₂ volume of the empty sample container was measured.
- 9- The absorbed amount of H₂ was calculated from the difference of measured volumes at 7 and 8.

Similar systems were used by Langohr *et al.* [17], Kawamura *et al.* [18], Muthukumar *et al.* [19].

The system pressure change was recorded during absorption experiments. An example of these records can be found in Fig. 7. For all samples the system pressure was attained to a certain pressure at approximately 260 minutes. Therefore, the absorption experiments were limited to 5 hours. Experiments were repeated twice.

Desorption

For all samples, the hydrogen release processes were performed at the temperature of 100°C and open to atmospheric pressure. The experimental procedures for desorption measurements are as follows:

- 1- After the absorption process, the sample container was isolated using the sample isolation valve. Then the needle valve, which was inserted between the sample container and the burette, was opened to measure the H₂ volume.

- 2- The sample container was gradually heated to 100°C (2°C/minute).
- 3- The system pressure change was recorded.
- 4- The releasing H₂ volume was recorded.
- 5- Procedures 1-5 were repeated and the H₂ volume of the empty sample container was measured once again.
- 6- The desorbed amount of H₂ was calculated from the difference of the measured volumes at 4 and 5.

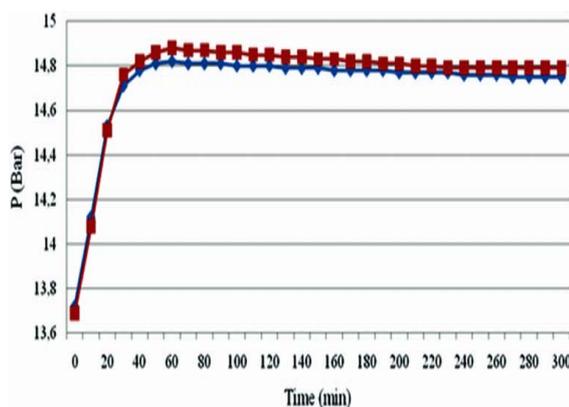


Fig. 7: System pressure change during the absorption experiment of Mg₁₇Al₁₂ pressed at 600MPa.

Conclusions

In this study three Mg-Al alloys; Al rich β -Mg₂Al₃, γ -Mg₁₇Al₁₂ and Mg rich Mg:Al (90:10) phases were tested for hydrogen storage and desorption. Performance studies were carried out by varying the alloy types and the pressing pressure levels of alloys. The composition of the alloys was changed during the pressing and sintering procedures. Upon XRD patterns, after the pressing and sintering, β -Mg₂Al₃ and Mg:Al (90:10) phases decomposed into γ -Mg₁₇Al₁₂, Mg and Al compositions. γ -Mg₁₇Al₁₂ was the main phase in the hydrogen adsorption/desorption process. Mg₂Al₃ alloy (pressed at 600MPa) stored approximately 0.37 wt.% hydrogen, while 200MPa stored 0.15 wt.% hydrogen. Pressing pressure levels and also the pore sizes of alloys had a significant effect on the absorption and desorption performance of hydrogen. Beside these, the addition of Al effected the dehydrogenation of alloys negatively due to its positive effect on the dehydrogenation energy.

Acknowledgements

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