Solid-State Synthesis of Hydrogen Storage \( \text{Mg}_2\text{Co} \) Alloys via Bulk Mechanical Alloying

Yijing Wang\(^1\), Tatsuhiko Aizawa\(^2\,*\) and Chikashi Nishimura\(^3\)

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1. Introduction

Magnesium alloys possess many advantageous functional properties and performance like high specific strength, vibration absorption, or high recyclability. In particular, much attention has been paid to investigating their high intrinsic hydrogenation and de-hydrogenation performance. In general, hydrogen storage materials are main targets of research and development in two major applications: negative electrodes for rechargeable batteries like Ni/MH, or, hydrogen storage devices for fuel cells of electric vehicles. Several important issues have to be considered for improvement of this performance: high hydrogen storage capacity, high kinetics in hydrogenation and de-hydrogenation processes, light weight and low cost. Magnesium base alloys are high-lighted as one of most promising candidate materials because of their relatively high functional capacities, low weight and recyclability, compared with LaNi\(_5\) and TiFe compounds.\(^1\) With respect to theoretical M/H ratio, \( \text{Mg}_2\text{CoH}_5 \) and \( \text{Mg}_2\text{FeH}_6 \) have higher hydrogen capacity than \( \text{Mg}_2\text{NiH}_4 \)\( ^{e.g.} \): 5.5 mass\% for \( \text{Mg}_2\text{FeH}_6 \), 4.5 mass\% for \( \text{Mg}_2\text{CoH}_5 \) and 3.6 mass\% for \( \text{Mg}_2\text{NiH}_4 \).\(^2\,3\) In the phase diagram of Mg–Ni system, there are two line compounds: hydrogen storage alloying phase, \( \text{Mg}_2\text{Ni} \) and laves-phase compound, \( \text{MgNi}_2 \). Except for corrosion resistance, hydrogenation of \( \text{Mg}_2\text{Ni} \) to \( \text{Mg}_2\text{NiH}_4 \) and de-hydrogenation to \( \text{Mg}_2\text{Ni} \) become a typical thermodynamic route for hydrogen storage capacity. On the other hand, Mg–Fe system has no compounds in its phase diagram so that non-traditional processing is needed to find one route from non-equilibrium metallic phase or the other route from a stable hydride of \( \text{Mg}_2\text{FeH}_5 \).

\( \text{Mg} \)-Co system has only one stable compound: laves phase, \( \text{Mg}_2\text{Co} \). Like Mg–Fe system, two approaches are theoretically considered to fabricate the hydrogen storage alloys in this system: 1) Search for a new route starting from \( \text{Mg}_2\text{CoH}_6 \) in de-hydrogenation, and, 2) New processing to synthesize a non-equilibrium metallic compound as a starting phase in hydrogenation. Even in the second approach, the conventional pyro-metallurgy processing is useless since the melting point of magnesium, 923 K, is far below that of cobalt, 1768 K. In addition, since magnesium has a very high vapor pressure; special precautions are indispensable to adjust the molar ratio to a targeting chemical composition. Normal solid state synthesis to form \( \text{Mg}_2\text{Ni} \) cannot be applied to synthesize \( \text{Mg}_2\text{Co} \). There are only a few reports on the formation of \( \text{Mg}_2\text{Co} \) by mechanical alloying method (MA) in the literature.\(^5\,6\) Bulk mechanical alloying (BMA) was successfully applied to solid-state synthesis of \( \text{Mg}_2\text{Ni} \) from elemental powder mixture.\(^7\) In addition to grain size refinement of \( \text{Mg}_2\text{Ni} \) to 5–10 nm, non-equilibration is accommodated to this solid-state synthesis of \( \text{Mg}_2\text{Ni} \) for \( 0 < x < 0.5 \) via BMA. This BMA process is driven by the repeated plastic deformation, flow and circulation by using the forging-type pass schedule in the die-set system for mixing, refining and alloying. It needs shorter process time, and has less or even no contamination which is an obstacle in solid-state reactions in the conventional repeated milling or attrition.\(^8\,9\)

In the present study, this BMA method is applied to fabrication of \( \text{Mg}_2\text{Co} \) alloy from the starting element constituent mixtures of magnesium and cobalt. This solid-state reaction process is first described by on-line measurement of imposed mechanical energy on BMA as well as XRD and DTA analyses. \( \text{Mg}_2\text{Co} \) is successfully synthesized in a single phase by this solid state reaction via bulk mechanical alloying (BMA) and annealing. This synthesized \( \text{Mg}_2\text{Co} \) is stable in relatively high temperature range; both holding temperature and hydrogen pressure are controlled in wider range to investigate its hydrogenation and de-hydrogenation behavior. Both DSC, PCT and XRD are used to describe the

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*Corresponding author, E-mail: aizawa@asiaseed.org
hydrogenation and de-hydrogenation processes starting from the annealed Mg₂Co.

2. Experimental Procedure

Pure elemental powders of magnesium and cobalt with the purity of 99.9% were prepared to have average particle size of 200 and 100 μm, respectively. Their mixture was weighed to be 23 g with a stoichiometric molar ratio of Mg₂Co, poured into a die cavity and subjected to BMA (bulk mechanical alloying). During BMA, the relative density was kept constant, 75% T.D. and no lubricants or additives were used. Nearly the same pass procedure as reported in Ref. 7) was utilized in the actual bulk mechanical alloying operation: two compression modes and one forward extrusion mode were employed as a loading sequence per cycle. The maximum applied load was limited by 550 kN. The number of cyclic loading (N) was varied from N = 0 to N = 2500 to describe the alloying process from elemental mixture to compounds with increasing N. Details in the forging facilities and loading schedule were found elsewhere. All through BMA, the sample material was processed in BMA at argon atmosphere and under forced cooling conditions.

The phase and structure of synthesized compounds was analyzed by a JEOL/JDX-3530 X-ray diffraction with the radiation of Cu Kα (λ = 0.15405 nm) at room temperature. Their microstructure was characterized by JEOL/JSM-5500LV scanning electron microscopy (SEM) and JED-2100 energy dispersive X-ray spectroscopy (EDS). Thermal analysis of the samples was made by differential scanning calorimetry (DSC). The heating rate was kept constant, 20 K/min up to 1073 K in the argon atmosphere when using Shimadzu DTG-60. Annealing process was employed to investigate thermal stability of the synthesized, non-equilibrium phase Mg₂Co and to determine the adequate annealing temperature. As-BMA samples by N = 2000 were annealed at 723 K for 3.6 ks to prepare for hydrogenation and de-hydrogenation experiments.

Hydrogenating and de-hydrogenating behavior was traced by a differential scanning calorimeter (DSC), TA instruments 2910 DSC V4.4E. The holding temperature was controlled to vary from 298 to 823 K in the heating sequence, then to be cooled to 373 K in hydrogen atmosphere, and to be heated again from 373 to 823 K. The heating rate was 8.33 × 10⁻² K/s (or 5 K/min), and cooling rate was 1.67 × 10⁻¹ K/s (or 10 K/min). The hydrogen pressures were controlled to be 0.5, 0.75, 1.0, 1.5, and 2.0 MPa. The experimental conditions were summarized in Table 1. The pressure-composition isotherms were also measured by the Sievert method at 633 K.

3. Results and Discussion

3.1 Solid-state formation of Mg₂Co

In the solid-state synthesis via BMA, the imposed mechanical energy during processing was found to be an indicator to describe the mixing, refining and alloying processes. From the online measured histories of displacement and applied load both for upper and lower punches in BMA, an input energy per cycle (W) was calculated by

<table>
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<th>Sample No.</th>
<th>Sample mass (mg)</th>
<th>Hydrogen pressure (MPa)</th>
<th>Heating rate (K/min)</th>
<th>Cooling rate (K/min)</th>
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</thead>
<tbody>
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<td>10</td>
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<td>2</td>
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<td>0.75</td>
<td>5</td>
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<tr>
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<td>1.0</td>
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<tr>
<td>5</td>
<td>12.26</td>
<td>2.0</td>
<td>5</td>
<td>10</td>
</tr>
</tbody>
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Fig. 1 Variation of energy per cycles with increasing the number of cycles in the bulk mechanical alloying.

\[ W = \int_{cycle} \left( P_{lower} \times \Delta \delta_{lower} + P_{upper} \times \Delta \delta_{upper} \right). \] (1)

where P is the applied load in BMA and δ, the measured stroke displacement, for both upper and lower punches. Since the equivalent strain rate and the sample volume are constant during BMA, this inner energy per cycle is only functional in the flow stress of materials. In the early stage of BMA, W is thought to increase slightly because of work hardening and to be nearly constant for refined mixture of elemental constituents.

Time history of W with the number of cycles, N, was shown in Fig. 1. During the initial stage up to 600 cycles, the input energy per cycle (W) was nearly constant, \( W = 5 \) kJ/cycle. That is, mixing and refining takes place up to \( N = 600 \) without solid-state reaction. W increased gradually from \( N = 600 \); e.g., \( W = 7 \) kJ at \( N = 800 \), 8 kJ at \( N = 1000 \) and 10 kJ at \( N = 1600 \). This proves that more mechanical energy is required to sustain the mechanically induced solid-state reaction during BMA. Figure 2 shows variation of XRD profiles with increasing N up to 2500. The intensities of diffraction peaks for magnesium and cobalt were gradually reduced with N. Peak broadening also took place with increasing N. Significant increase of W in the above corresponds to commencement of solid-state reaction to Mg₂Co.

The solid-state reaction behavior is also described by DTA. Figure 3 depicted the variation of measured DTA diagrams at each specified number of cycles. An exothermic
A peak was detected near the endothermic peak around the melting temperature of magnesium when $N = 0$ in Fig. 3. This DTA diagram implies that exothermic reaction takes place from elemental mixture to MgCo$_2$ and that residual magnesium melts at $T = 923$ K. The exothermic peak intensity reduced gradually with $N$, and, the peak temperature shifted itself to lower temperature side due to grain size refinement by BMA. When $N = 1500$, no peaks were detected in DTA. Figure 4 shows the SEM micrograph of synthesized as-BMA sample by $N = 2000$. No cobalt phases were apparently seen.

Annealing process was employed to investigate the thermal stability of synthesized non-equilibrium phase, Mg$_2$Co via BMA. Figure 5 shows the variation of XRD profiles with increasing the annealing temperature ($T_A$). When $T_A < 623$ K, little changes were detected in phase and structure; several peaks of crystalline Mg$_2$Co were seen together with a broad peak. This assures that as-BMA Mg$_2$Co is a mixture of crystalline and amorphous phases. When $T_A > 623$ K, the characteristic diffraction peaks (111) and (511) were detected at $2\theta \approx 13.32^\circ$ and $2\theta \approx 40.94^\circ$, respectively. Lattice parameters of this stable compound were calculated from these peaks: $a = 1.144$ nm in the face-center-cubic structure. This is in good agreement with the reference data for Mg$_2$Co reported in Ref. 12): $a = 1.143$ nm. Annealing process is needed to further make reaction of the amorphous Mg$_2$Co to crystalline one.

This synthesized Mg$_2$Co is stable up to $T_A = 833$ K since its characteristic peaks were dominant in these XRD patterns for $T_A < 833$ K. Peaks to MgCo$_2$ as well as other small peaks for magnesium were detected at $T_A = 853$ K. This assures that the solid-state synthesized Mg$_2$Co is actually a non-equilibrium phase to be decomposed and reacted to final stable phase by exceeding $T_A$ over the critical temperature. Since the decomposition reaction from Mg$_2$Co to MgCo$_2$ and Mg takes place in local and in partial, exothermic peaks to this decomposition process cannot be seen in Fig. 3 for $T > 833$ K.

The whole as-BMA powders by $N = 2000$ were annealed at 723 K for 3.6 ks to prepare the single phase Mg$_2$Co compound samples for the following hydrogenation and dehydrogenation tests. In these tests, maximum temperature in
heating and cooling sequences is kept to be below this critical temperature in order to preserve the single metallic phase.

### 3.2 Hydrogenation and de-hydrogenation behavior

DSC was employed to describe the hydrogenation and de-hydrogenation behavior of the solid-synthesized Mg$_2$Co for various hydrogen pressure $P$. Figure 6 shows typical DSC curves in heating and cooling sequences when $P$ is kept constant, $P = 0.5$ and $2.0$ MPa, respectively. These measured DSC curves are characterized by several exothermic and endothermic peaks. For example, one exothermic peak #1 as well as two endothermic peaks #2 and #3 are detected in heating sequence, and, two exothermic peaks #4 and #5 are seen in cooling sequence for a sample-1 in Fig. 6(a). In case of sample-5, only peaks #1 to #4 are seen in Fig. 6(b). That is, peaks #1, #4 and #5 denote for hydrogen absorption reactions while peaks #2 and #3, for hydrogen desorption reaction, respectively. Table 2 summarizes the onset temperatures of the whole hydrogenation and de-hydrogenation steps for #1 to #4.

Figure 7 describes the effect of holding hydrogen pressure on the hydrogenation and de-hydrogenation reaction during the heating sequence. Since the peak #1 shifts to lower temperature side with increasing $P$, this hydrogenation step #1 commences at lower temperature in higher hydrogen pressures. On the other hand, onset temperatures for two desorption reaction steps #2 and #3 increase with increasing $P$. Figure 8 also shows the effect of hydrogen pressure on the hydrogenation in cooling sequence. Corresponding to increase of onset temperature for de-hydrogenation with $P$, onset temperature for hydrogenation increases itself with $P$.

To be noticed, there are three peaks for hydrogenation: peak #5, hydrogenation step in lower hydrogen pressure range, peak #1, hydrogenation step in the lower temperature range, and, peak #4, hydrogenation step in the higher temperature range. This implies that hydrogenation process does never take place in a single-step reaction like 2Mg$_2$Co + 5H$_2$ → 2MgH$_2$CoH$_5$. In particular, since the hydrogenation step by #4 only works for $T > 650$ K, the hydrogenation process is thought to take place in two steps at lower holding temperature range. Figure 9 summarizes the hydrogen pressure dependency of hydrogenation and de-hydrogenation reactions. This suggests that hydrogenation process is mainly governed by two steps corresponding to peaks #1 and #4 and de-hydrogenation process is also described by two reactions corresponding to peak #2 and #3.

According to this temperature dependency of hydrogenation and de-hydrogenation processes, the hydrogen absorption and desorption capacity of Mg$_2$Co is strongly affected by the holding temperature ($T_H$). For example, when $T_H =$
633 K, the hydrogenation process first starts in step #5 with relatively large hydrogen absorption. It is followed by the hydrogenation step #1 with relatively sluggish absorption rate against $P$. The de-hydrogenation process is only governed by step #2 with prompt rate against $P$. Figure 10 shows the PCT-curve (pressure-content isotherm) of annealed Mg$_2$Co, measured at $T_H = 633$ K. In accordance to the above prediction from Fig. 9, this PCT curve has two plateau pressures in the hydrogenation process and one plateau pressure in the de-hydrogenation process.

Figure 11 reveals that the final product after hydrogenating the annealed Mg$_2$Co is Mg$_2$CoH$_5$. The calculated lattice parameters from this XRD profile is: $a = 0.488$ nm and $c = 0.661$ nm for a tetragonal phase. These are found to be in good agreement with reference data. To describe this stepwise reaction, XRD profiles for starting Mg$_2$Co phase and samples after the first and second plateaus were compared in Fig. 12. Intermediate hydrides of Mg$_2$Co were first synthesized before final reaction to Mg$_2$CoH$_5$. Since no phases were seen for MgH$_2$, Co and MgCo$_2$, no disproportionation reaction is thought to take place in this hydrogenation process.

The maximum hydrogen absorption capacity of this Mg$_2$Co is limited by 2.03 mass%, which is much lower than the theoretical value of Mg$_2$CoH$_5$, 4.5 mass%. Hydrogenation step #4 and de-hydrogenation step #3 are absent in the thermodynamic route at $T_H = 633$ K. In other words, higher holding temperature is needed to activate the whole reaction steps both for hydrogenation and de-hydrogenation. Although cobalt phase is never detected in Figs. 3 to 5, the presence of residual cobalt with secondary phases could reduce the hydrogen capacity. Hence, purity of Mg$_2$Co must be further improved and synthesized Mg$_2$Co must be chemically modified to significantly increase the maximum hydrogen storage capacity.
4. Conclusion

Mg$_2$Co was successfully synthesized by the solid state reaction from the Mg and Co powder mixture via bulk mechanical alloying (BMA) and annealing. The synthesized Mg$_2$Co is stable up to 833 K. The lattice parameters of the cubic Mg$_2$Co compound ($a = 1.144$ nm) were in good agreement with reference data. Hydrogenation process of Mg$_2$Co is composed of two or three steps and de-hydrogenation process of Mg$_2$CoH$_5$, two steps. The first hydrogenation step commences at relatively low temperature and higher holding temperature is needed to activate the following steps. Since Mg$_2$CoH$_5$ is a stable hydride, de-hydrogenation takes place only at higher temperature. In case when the hydrogenation and de-hydrogenation steps, working at higher temperatures, are excluded in the thermodynamic route at 633 K, the maximum hydrogen absorption is limited to 2.03 mass% lower than the theoretical amount. Hence, relatively high holding temperature is still necessary to obtain maximum hydrogen absorption equivalent to theoretical capacity for Mg$_2$Co without chemical modifications.

REFERENCES

12) Joint Committee of Powder Diffraction Standards card (JCPDS) 44-1149.