

## SYNTHESIS OF $Mg_2FeH_6$ , $Mg_2CoH_5$ AND $Mg_2NiH_4$ BY HIGH-PRESSURE SINTERING OF THE ELEMENTS

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**Abstract**—The title compounds were synthesized by sintering mixtures of fine metal powders at optimized experimental conditions of temperature (450–500°C) and hydrogen pressure (90 bar). In contrast to previous work, nearly single-phase samples of up to 10 g were obtained in a single-step process.

### 1. INTRODUCTION

Magnesium based transition metal hydrides are of interest for hydrogen storage [1]. However, compounds such as  $Mg_2NiH_4$  [2],  $Mg_2CoH_5$  [3] and  $Mg_2FeH_6$  [4] are not easy to synthesize as single-phase samples. Monoclinic  $Mg_2NiH_4$  is usually prepared by hydrogenation of commercially available alloys such as HYSTOR 301 (Ergenics, Inc., Div. of MPD Technology Corp., Ringwood, NJ, U.S.A.) that contain the intermetallic compound  $Mg_2Ni$  together with impurity phases such as Mg or  $MgNi_2$ . Consequently, the hydrided alloy contains  $Mg_2NiH_4$ ,  $MgH_2$  or  $MgNi_2$ . Tetragonal  $Mg_2CoH_5$  and cubic  $Mg_2FeH_6$  cannot be synthesized from binary Mg–Co and Mg–Fe alloys because stable intermetallic compounds do not exist in these systems. In the past these hydrides were synthesized by a sintering technique from elemental powder mixtures [3, 4]. The technique was not optimized and resulted in multi-phase samples that contained more or less large amounts of impurity phases such as  $MgH_2$ , unreacted Fe and Co, and other unidentified phases. Thus the samples had to be purified by a tedious multi-step procedure [3, 4].

In this communication we describe improved experimental conditions that allow the synthesis of these ternary metal hydrides as nearly single-phase samples in a single-step process.

### 2. EXPERIMENTAL

#### Materials

The characteristics of the metal powders used for the synthesis are given in Table 1. Note that magnesium powders of various particle size were used from four different suppliers. High-purity hydrogen (99.9999%; Carba gas, Switzerland) was used for the hydriding reactions.

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#### Apparatus

All reactions were done in a high-pressure autoclave (Parr Instruments Co., U.S.A., type-4652, inside diameter 2.5 inches, capacity 500 ml) made of a special stainless steel (T316-SS), and supporting hydrogen pressures of up to 150 bar at temperatures of up to 600°C. The vessel has a full opening head and split-ring closures, and was heated by an external furnace. The sealing force was developed by tightening eight screws which bear against a silver plated stainless steel gasket. Accidental overpressure is avoided by a safety rupture disc installed in the head of the reactor.

#### Synthesis

Intimately mixed metal powders of Mg–Fe, Mg–Co and Mg–Ni at the compositional ratio 2:1 were pressed under 3 tons to cylindrical pellets, each pellet weighing about 0.5 g and measuring 5–7 mm in height and 4 mm in diameter. The pellets were enclosed in nickel crucibles (B-J Scientific Products, Inc., U.S.A.) having a capacity of about 10 ml (diameter 27 mm, height 22 mm, wall thickness 1 mm). Each crucible was filled with two pellets. Batches of up to ten crucibles were put into the autoclave, corresponding to a total sample weight of about 14 g (~10 g for Mg–Fe, and ~2 g each for Mg–Co and Mg–Ni). During the preliminary stage of the work alumina crucibles and quartz tubes were used.

Table 1. Characteristics of starting elements

Sample	Purity (%)	Particle size (mesh)	Firm
Magnesium	99.6	–400	Cerac
Magnesium	99.8	50	Ventron
Magnesium	99.8	50–150	Fluka
Magnesium	99.5	50–150	Heraeus
Iron	99.999	–60	Johnson Matthey
Cobalt	99.998	–20	Merck
Nickel	99.5	–100	Johnson Matthey

They were later abandoned because the former turned out to be difficult to clean after the hydriding reaction, and the latter could not be reused.

The samples were activated by degassing the autoclave to  $10^{-2}$  mbar at room temperature and flushing it with hydrogen. After several such cycles, the autoclave was filled with hydrogen at various pressures at room temperature and heated to the following temperatures and pressures: 350°C at initial (final) pressures 11 (15), 30 (50), 55 (90), 65 (120) bar; 400°C at initial (final) pressures 9 (15), 27 (50), 47 (90), 65 (120) bar; 450°C at initial (final) pressures 8 (15), 24 (50), 40 (90) bar; 500°C at initial (final) pressures 6 (15), 20 (50), 35 (90) bar. The autoclave was kept at these temperatures for up to 10 days, then cooled to room temperature, and opened to air after releasing the hydrogen pressure. The previously compacted pellets had disintegrated into fine powders that had strongly expanded. The largest expansion (by a factor of 2–3) occurred with Mg–Fe which completely filled the crucibles. In order to prevent spontaneous ignition of these samples a stream of protective Ar gas was passed over the crucibles during their transfer into an Ar filled glove box.

#### Characterization

All samples of each batch were examined by X-ray powder diffraction methods at room temperature. The measurements on cubic  $\text{Mg}_2\text{FeH}_6$  and tetragonal  $\text{Mg}_2\text{CoH}_5$  were performed on a Guinier camera (ENRAF-NONIUS) by using Co  $K_\alpha$  radiation ( $\lambda = 1.79026 \text{ \AA}$ ), and those on monoclinic  $\text{Mg}_2\text{NiH}_4$  on a conventional X-ray powder diffractometer by using Ni filtered Cu  $K_\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). Representative examples for such patterns are represented in Fig. 1. All patterns were taken on powders to which small quantities of silicon ( $a = 5.4308 \text{ \AA}$ ) were added as an internal standard. Lattice parameters were refined from corrected line positions by using the computer program LATCON [5]. They are summarized in Table 2.

### 3. RESULTS AND DISCUSSION

The synthesis of single-phase samples was found to depend mainly on the nature of the starting materials, the reaction pressure, the reaction temperature, and the reaction time. A most important factor was the nature of the Mg powder. Among the different powders used (see Table 1) only the very fine powder supplied by Cerac products (–400 mesh) yielded single-phase samples at short reaction times. Thus all subsequent experiments were done by using this powder. The conditions of pressure and temperature were also important. The formation of single-phase samples required pressures of at least 90 bars and temperatures of at least 450°C. For the iron-based samples low-pressure conditions (450–500°C; 15 bar; 7–10 days) did not allow the reaction to proceed to completion, yielding  $\text{Mg}_2\text{FeH}_6$ ,  $\text{MgH}_2$  and metallic Fe. For the cobalt-based samples low-pressure conditions (450–500°C; 15 bar; 7–10 days) resulted in the formation of the intermetallic compound

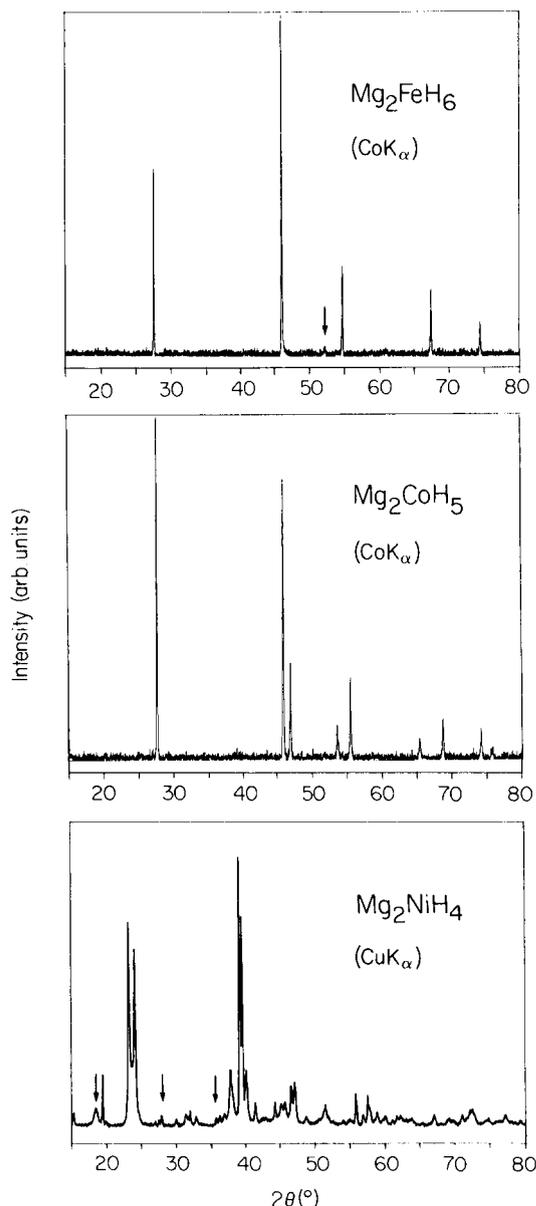


Fig. 1. X-Ray powder diffraction patterns of: (a)  $\text{Mg}_2\text{FeH}_6$ , (b)  $\text{Mg}_2\text{CoH}_5$  (optical densitometer traces of Guinier films) and (c)  $\text{Mg}_2\text{NiH}_4$  (diffractometer trace). Peaks due to impurity phases are marked by arrows.

$\text{MgCo}_2$  and two novel ternary metal hydride phases, one having cubic symmetry and approximate composition  $\text{Mg}_2\text{CoH}_x$  [6], and the other having orthorhombic symmetry and approximate composition  $\text{Mg}_3\text{CoH}_x$  [6, 7]. Intermediate-pressure conditions (450–500°C; 50 bar; 7–10 days) lead to the formation of tetragonal  $\text{Mg}_2\text{CoH}_5$  and orthorhombic  $\text{Mg}_3\text{CoH}_x$ . The influence of temperature was less critical than that of pressure, and appeared to influence mainly the kinetics of the reactions. In the

Table 2. Structural data for the ternary hydrides

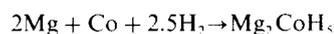
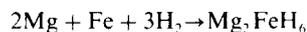
Hydride	Symmetry	Lattice parameters (Å)		
		This work	Earlier work	(Ref.)
Mg <sub>2</sub> FeH <sub>6</sub>	Cubic	<i>a</i> = 6.4287(7)	6.443(1)	4
Mg <sub>2</sub> CoH <sub>5</sub>	Tetragonal	<i>a</i> = 4.4745(7)	4.480(2)	3
		<i>c</i> = 6.611(2)	6.619(3)	
Mg <sub>2</sub> NiH <sub>4</sub>	Monoclinic	<i>a</i> = 14.3688(9)	14.363(2)	8
		<i>b</i> = 6.4063(8)	6.4052(5)	
		<i>c</i> = 6.4918(6)	6.4863(6)	
		<i>β</i> = 113.54(1)°	113.633(2)	

iron-based samples, for example, reaction temperatures lower than 450°C lead to incomplete reactions even at high pressure (120 bar) and long reaction times (10 days), yielding Mg<sub>2</sub>FeH<sub>6</sub>, MgH<sub>2</sub> and Fe. As to the influence of the reaction time, periods shorter than 2–3 days always lead to incomplete reactions, i.e. to mixtures of phases. Finally, the volume and temperature gradient of the reactor vessel used limited the sample weight to about 20 g.

The most convenient experimental conditions to obtain Mg<sub>2</sub>FeH<sub>6</sub>, Mg<sub>2</sub>CoH<sub>5</sub> and Mg<sub>2</sub>NiH<sub>4</sub> powders of high yield (up to 10 g) were found to be around 90 bar and 450°C. The powders have green (Mg<sub>2</sub>FeH<sub>6</sub>), black/dark grey (Mg<sub>2</sub>CoH<sub>5</sub>), and reddish-brown (Mg<sub>2</sub>NiH<sub>4</sub>) color, and were practically single-phase as judged from X-ray powder photographs (Fig. 1). Except for one small peak in the Mg<sub>2</sub>FeH<sub>6</sub> pattern due to unreacted iron, and very small peaks in the Mg<sub>2</sub>NiH<sub>4</sub> pattern due to MgH<sub>2</sub> and Mg(OH)<sub>2</sub> (all marked by arrows in Fig. 1), the patterns correspond to those calculated for the respective ternary phases. The refined lattice parameters (Table 2) are consistent with those reported for monoclinic Mg<sub>2</sub>NiH<sub>4</sub>

[3] and tetragonal Mg<sub>2</sub>CoH<sub>5</sub> [4]. The value for cubic Mg<sub>2</sub>FeH<sub>6</sub> differs significantly from earlier neutron diffraction data [4], but is judged to be more reliable because of the use of a silicon standard.

In conclusion, we have presented improved experimental conditions for the solid state reactions



The ternary metal hydrides are obtained in a single-step process having a satisfactory yield.

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