

Synthesis and hydrogen storage behavior of Mg–Co–H system at nanometer scale

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Abstract

There are few reports on the hydrogen storage behavior study of Mg–Co–H system in the literature, although Mg₂CoH₅ has a much higher hydrogen capacity than Mg₂NiH₄. This is due to the great difficulty in the synthesis of Mg₂CoH₅ and Mg₂Co in convenient conditions. Here we successfully synthesized the nanostructured Mg₂CoH₅ and Mg₂Co from Mg and Co nanoparticles prepared by hydrogen plasma–metal reaction method. The reaction mechanism of the synthesis of the Mg–Co–H system was studied. The morphology of the Mg–Co–H system in nanometer scale was observed. The hydrogen absorption curves and the pressure–composition isotherm (*P–C–T*) properties of the Mg–Co–H system were studied. The van't Hoff equations and the formation enthalpies and entropies of the produced Mg₂CoH₅ and Mg₃CoH₅ were obtained. The results were discussed by comparing with the corresponding ones of Mg–Co–H system by other groups and the ones of nanostructured Mg–H and Mg–Ni–H systems by our group.

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Keywords: Hydrogen storage; Nanostructure; Mg–Co–H system

1. Introduction

Mg-based alloys have attracted great interest because of their high hydrogen storage capacity, light weight and great abundance, and are thought to be the most promising candidates for hydrogen storage use in the future. The hydrogen storage capacities in the common Mg-based metal hydrides are 3.6, 4.5 and 5.4 wt% for Mg₂NiH₄, Mg₂CoH₅, and Mg₂FeH₆, respectively. However, a very interesting aspect is that since Reilly and Wiswall found and studied the hydrogen storage properties of Mg₂Ni in 1968 [1], thousands of articles on Mg–Ni–H system have appeared, while there are only tens of articles published on Mg–Co–H: in 1947, Cramer et al. reported that Mg₂Co can store a larger amount of hydrogen [2]. This phenomenon can be explained based on this vital point: greater difficulty in

the synthesis of Mg₂Co. Although it is also difficult to prepare stoichiometric Mg₂Ni compound for the great difference in vapor pressure and melting point between Mg and Ni, many methods have been developed, such as conventional melting [1], mechanical alloying (MA) [3,4], combustion synthesis [5], melting spinning [6], replacement-diffusion method [7] and rotation-cylinder method [8]. When it comes to Mg₂Co, things are quite different. The first confirmed result about Mg₂Co compound was reported by Konstanchuk et al. [9,10] and their XRD result is still being used as the Powder Diffraction File (JCPDS 44-1149). As in many other groups, they produced the Mg₂Co sample with a large content of several impurity phases by dehydrogenating the Mg₂CoH₅ sample, which is produced by sintering or MA in a hydrogen atmosphere. They thought Mg_xCo could not be obtained either by melting or by MA. This is a bit incorrect because Bobet et al. [11] obtained Mg₂Co (purity about 80 wt%) by MA method, although the process seemed to be a little difficult (milled for 150 h and annealed for 8 days).

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We have conducted some research on pure Mg [12] and Mg_2Ni compound [13–15] in nanometer scales, by using Mg and Ni nanoparticles prepared by hydrogen plasma–metal reaction (HPMR) method. We found that Mg_2Ni can be prepared in quite convenient conditions due to the use of original Mg and Ni nanoparticles and the nanostructured hydrogen storage materials can greatly improve the hydrogen absorption properties because of the small size and large specific surface area of the particles, which means that more area can be easily exposed to hydrogen atmosphere and more nucleation sites for metal hydrides can be obtained. Here we studied, in a similar but more detailed way, the synthesis and hydrogen storage properties of the Mg–Co–H system at a nanometer scale. Because of the use of nanostructured materials, we obtained some new and novel results. Some of them, such as the hydrogen absorption rate curves and the reaction mechanism study of different hydrogen storage behaviors of the Mg–Co–H system have never been reported by others.

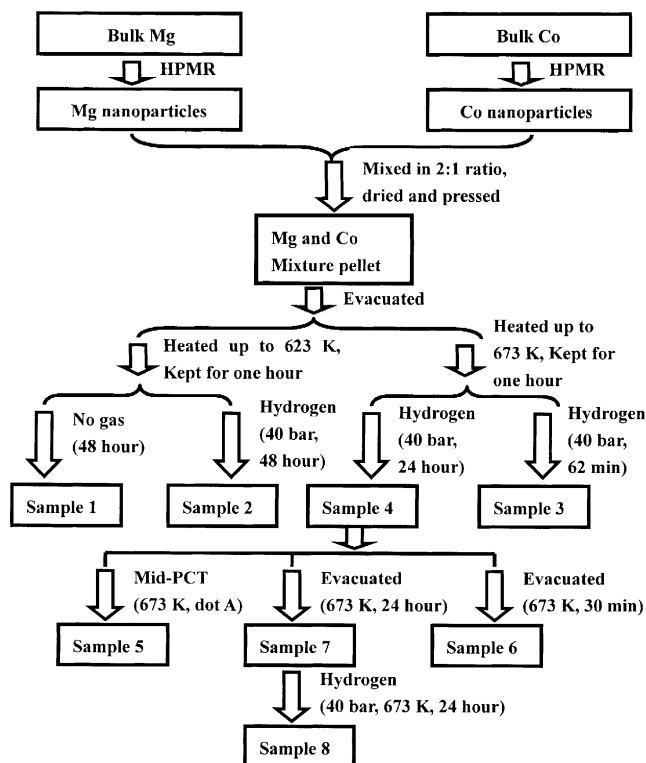
2. Experimental details

2.1. Preparation of Mg and Co nanoparticles

A schematic illustration of the experimental equipment, which was used for production of Mg and Co nanoparticles by HPMR method, is shown here [14]. Mg and Co nanoparticles were produced by arc melting bulk Mg (purity >99.9%) and Co (purity >99.5%) in mixture of 50% Ar and 50% H_2 gas of 1 bar. The flow rate of the circulation gas for collection of nanoparticles was 100 L/min. The arc voltage and arc current were 25 V and 250–300 A, respectively. Before the Mg and Co nanoparticles were taken out from the reaction chamber, they were passivated with a mixture of argon and air to prevent the particles from burning.

2.2. Synthesis of Mg_2CoH_5 and Mg_2Co nanoparticles

A mixture of Mg and Co nanoparticles in 2:1 molar ratio was put in acetone and then mixed by an ultrasonic homogenizer for 30 min (15 min every time, twice). After having dried in the air naturally, the mixture was pressed at 750 bar by a press for 30 s into pellets of about 13 mm in diameter, 0.3 mm in height and 0.1 g in weight, as the samples for the synthesis reaction of Mg_2CoH_5 and Mg_2Co compound. Scheme 1 shows the preparation procedures of different samples (samples 1–8). After the Mg and Co nanoparticle mixture sample was put into a reactor, the system was evacuated to 10^{-3} Pa. After the mixture sample was heated up to 623 K, kept for 49 h and then cooled to room temperature, we obtained sample 1 (called “S1”, hereafter). When the mixture sample was heated up to 623 K, kept for 1 h, and then a



Scheme 1. Preparation procedures of samples 1–8 (S1–S8).

hydrogen atmosphere of about 40 bar was provided and kept for 48 h, we obtained sample 2 (S2) after the system was cooled to room temperature. After the mixture sample was heated up to 673 K, kept for 1 h, and then a hydrogen atmosphere of 40 bar was provided, we began to measure the hydrogen absorption rate of the $2Mg+Co$ nanoparticle mixture sample. After 62 min of measurement, the system was cooled to room temperatures quickly and to obtain sample 3 (S3). If we did not cool the system after the hydrogen absorption rate measurement and kept it at 673 K for 24 h, we obtained sample 4 (S4) after it was cooled. After the first desorption equilibrium plateau of S4 at 673 K (see dot A in Fig. 5), we stopped the pressure–composition isotherm ($P-C-T$) measurement and cooled the system to room temperature quickly in 5 min to obtain sample 5 (S5). S4 was evacuated at 673 K for 30 min and then cooled to obtain sample 6 (S6); S4 was evacuated at 673 K for 24 h and then cooled to obtain sample 7 (S7). S7 was provided a hydrogen atmosphere of 40 bar at 673 K, kept for 24 h and cooled to room temperature to obtain sample 8 (S8).

2.3. Characterization and measurements

The structural analysis of the different samples was carried out by X-ray diffraction (XRD) using an automatic Rigaku X-ray diffractometer with monochromatic $CuK\alpha$ radiation at a scanning rate of $4^\circ/\text{min}$. The

measurements were carried out using a generator voltage of 40 kV and a current of 100 mA. The size distribution and morphology of the samples were observed by transmission electron microscopy (TEM) on a JEM-200CX operating at 160 KV.

A conventional pressure–volume–temperature technique, which means measuring hydrogen content versus time by recording the change of gas pressure in a constant volume, was used to obtain the hydrogen absorption curves and the P – C – T curves of the Mg–Co–H system at different temperatures. The hydrogen absorption and desorption measurements will be stopped when the change of hydrogen pressure is smaller than 10 Pa every second, though the hydrogen absorption or desorption reaction has perhaps not reached the equilibrium completely.

3. Results and discussion

3.1. XRD patterns and reaction mechanism of Mg–Co–H system

XRD results of different samples of Mg–Co–H system are shown in Fig. 1 and the composition and content results of S1–S8 are listed in Table 1. Fig. 1(a) is the Mg nanoparticle sample prepared by HPMR method. The main phase is Mg (JCPDS 35-0821, space group: $P6_3/mmc$, $a = 3.2136(3)$ Å, $c = 5.2113(2)$ Å). There is

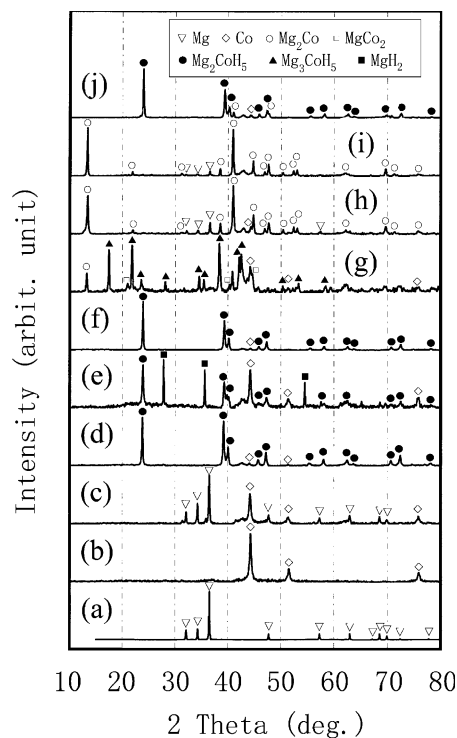


Fig. 1. XRD patterns of: (a) Mg nanoparticles, (b) Co nanoparticles, (c) S1, (d) S2, (e) S3, (f) S4, (g) S5, (h) S6, (i) S7, and (j) S8.

Table 1

Composition results of samples 1–8 (S1–S8) from XRD patterns

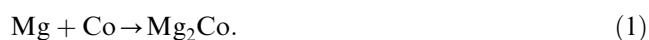
Sample	Composition (wt%)
S1	Mg (43%), Co (53%), unknown (4%)
S2	Mg ₂ CoH ₅ (97%), Co (3%)
S3	Mg ₂ CoH ₅ (42%), Co (32%), MgH ₂ (26%)
S4	Mg ₂ CoH ₅ (97%), Co (3%)
S5	Mg ₂ Co (22%), MgCo ₂ (10%), Mg ₃ CoH ₅ (60%), Co (8%)
S6	Mg ₂ Co (87%), Mg (8%), Co (5%)
S7	Mg ₂ Co (96%), Mg (4%)
S8	Mg ₂ CoH ₅ (92%), Mg ₂ Co (5%), Co (3%)

a very weak peak observed at $2\theta = 42.8^\circ$, which corresponds to the MgO phase. It was formed when the Mg nanoparticles were passivated with a mixture of argon and air. The MgO layer in the surface of the Mg nanoparticles can effectively prevent further oxidation of the Mg particles. Fig. 1(b) shows that there is only a Co phase (JCPDS 15-0806, space group: $Fm\bar{3}m$, $a = 3.5426(3)$ Å) in the sample. The main phases of S1 (Fig. 1(c), Table 1) are Mg and Co and there is no Mg₂Co trace in Fig. 1(c). From Fig. 1(d) and Table 1, we can see that the main phase of S2 is Mg₂CoH₅ (JCPDS 44-1160, tetragonal, $a = 4.4752(2)$ Å, $c = 6.6056(3)$ Å) and there is a little Co (3 wt%) in S2. The content of Co is calculated by comparing the changes of peak intensity in S2 and the mixture sample of S2 with pure Co. There is also a small MgO peak at 42.8° . The MgO impurity phase is formed due to the fresh surface that has been made during the hydriding/dehydriding reaction. The new surface makes the magnesium sample easier to be oxidated after it is taken out from the autoclave. The MgO impurity could not be formed in the preparation process, because the system is always in a very reductive condition of high temperature (>600 K) and high hydrogen pressure atmosphere (40 bar). So we have not calculated the MgO impurity content (varied from 1 to 5 wt%) in S1–S8. A similar result is achieved in S4 (Fig. 1(f)), which is at 673 K for 24 h. Zolliker et al. [16] obtained Mg₂CoH₅ with a purity of about 75% through a sintering technique in a condition of 690–720 K, 40–60 bar hydrogen atmosphere and several days. Selvam et al. [17] obtained nearly pure Mg₂CoH₅ sample by high-pressure sintering in conditions of about 90 bar, 723 K and more than 7 days. Ivanov et al. [10] prepared the Mg₂CoH₅ sample with some MgH₂, Mg and Co impurities by ball-milling for 2–3 days followed with sintering technique. Huot et al. [18] prepared the Mg₂CoH₅ sample with a purity of about 30% by MA under argon or hydrogen for 20 h and then sintering at 623 K, under 50 bar hydrogen atmosphere for 1 day. Now we obtained the Mg₂CoH₅ samples (S2 and S4) with a purity of 97 wt% in more convenient conditions (623 K, 40 bar hydrogen, 48 h or 673 K, 40 bar hydrogen, 24 h). Nanometer structure

effect plays an important role in the synthesis of Mg_2CoH_5 from Mg and Co nanoparticles in such simple conditions. Nanoparticles have a lower melting point because of the small size and large specific surface area of the particles, which implies the possibility of preparing Mg_2CoH_5 by using Mg and Co nanoparticles in hydrogen atmosphere. A similar phenomenon has been found in our Mg–Ni–H system [14]. The main phases of S3 (Fig. 1(e)) are Mg_2CoH_5 , Co and MgH_2 (JCPDS 12-0697, space group: $P4_2/mnm$, $a = 4.5174(3) \text{ \AA}$, $c = 3.0204(2) \text{ \AA}$).

Starting from S4, three samples (S5–S7) are obtained in different conditions. We find Mg_2Co (JCPDS 44-1149, Face-centered, $a = 11.4371(4) \text{ \AA}$), MgCo_2 (JCPDS 29-0486, space group: $P6_3/mmc$, $a = 4.8594(2) \text{ \AA}$, $c = 7.9276(1) \text{ \AA}$), Mg_3CoH_5 (JCPDS 44-1148, orthorhombic, $a = 4.6738(1) \text{ \AA}$, $b = 8.0754(3) \text{ \AA}$, $c = 10.0918(3) \text{ \AA}$) and Co phases in S5 (Fig. 1(g), more detailed discussion about Mg_3CoH_5 will appear at the hydrogen storage behavior part of this paper). Both S6 (Fig. 1(h)) and S7 (Fig. 1(i)) have the Mg_2Co and Mg phases. The difference between them is that in S6 there is a little Co phase, which can hardly be observed in S7. The Mg impurity in S7 is about 4 wt%, which is calculated in a similar way in S2 by comparing the changes of peak intensity in S7 and the mixture sample of S7 with pure Mg. Ivanov et al. [10] obtained the Mg_2Co sample by thermal decomposition of Mg–Co hydrides under vacuum for 4 days at temperatures between 698 and 723 K, with some Mg and Co impurities, which were very difficult to separate from the Mg_2Co phase. Almost all the Mg_2Co samples reported were prepared by dehydrogenation of Mg_2CoH_5 , except the one by Bobet et al. [11]. They obtained Mg_2Co (purity about 80 wt%) by MA method (150 h) followed by an annealing process (723 K, 8 days). They obtained a better result [19] by ball milling $2\text{Mg} + 0.8\text{Co} + 0.2 \text{ Ni}$ for 150 h and annealing the obtained sample at the same temperature for 4 days. The yield of Mg_2Co phase was 91 wt% and the impurities included Mg, Ni and Mg_2Ni . We obtained the Mg_2Co sample (S7) with a purity of 94 wt% through a simple hydrogen absorption and evacuation process at 673 K for about 48 h in all. From Fig. 1(j), we can find that the main phase in S8 is Mg_2CoH_5 and there is a little Mg_2Co and Co.

Comparing S1 with S2, we can conclude that at 623 K, Mg and Co cannot react to form Mg_2Co directly as in Eq. (1)



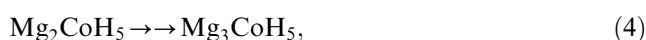
Comparing S3 with S4, we can conclude that when the heated Mg and Co mixture sample is provided with a hydrogen atmosphere, the first reaction will be (2)



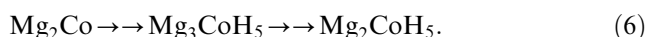
and the second reaction (3)



From S4 to S7 (S4→S5→S6→S7), mainly from Mg_2CoH_5 to Mg_2Co , it is hard to figure out the exact reaction mechanism because of the complicated intermediates including MgCo_2 , Mg_3CoH_5 , Co and Mg. Deeper research work needs to be carried out to give a detailed depiction of the process from S4 to S7. But from S6 to S7, there must be reaction (1). This has been proved by heating Mg and Co nanoparticles mixture at 673 K for about 24 h. Considering the result in S1, we can conclude that reaction (1) is likely to take place at a temperature between 623 and 673 K. The main reactions from S4 to S7 are thought to be Eqs. (4) and (5):



When the Mg_2Co absorbs hydrogen again at 673 K, the main reaction will be



3.2. TEM observation

The Mg nanoparticles (Fig. 2(a)) are hexagonal in structure with an average particle size of about 200–300 nm. The small particles are about several nanometers. The Co nanoparticles have a granular structure and the particle size ranges from 5 to 60 nm with an average size of about 30 nm. The Mg particles are bigger than the Co ones because of the higher generation rate of Mg by HPMR. This phenomenon has been well discussed by Ohno et al. [20]. From Fig. 2(c), we can observe that the Mg_2CoH_5 particle size ranges mainly from 50 to 300 nm and the average size is about 150 nm. The inserted electron diffraction pattern that has been

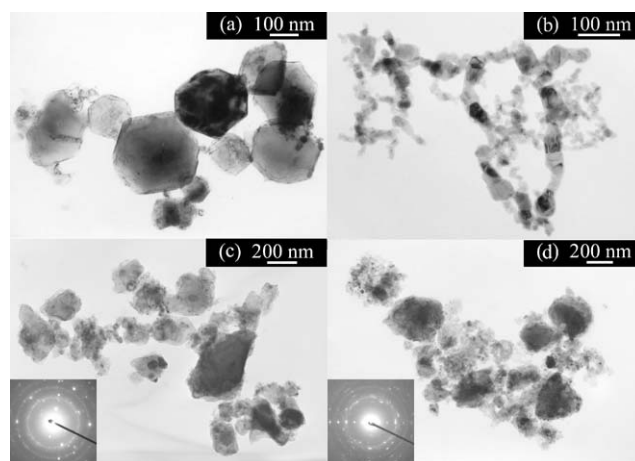


Fig. 2. Bright-field electron micrographs of (a) Mg nanoparticles, (b) Co nanoparticles, (c) Mg_2CoH_5 nanoparticles, and (d) Mg_2Co nanoparticles (inset: electron diffraction patterns).

successfully labeled confirms the main compound in S4 is Mg_2CoH_5 . The Mg_2Co particle size in Fig. 2(d) ranges mainly from 10 to 300 nm and the smallest ones are about 1–5 nm. The average size is about 150 nm. Comparing with the corresponding result of about 30–50 nm in Mg–Ni–H system [15], higher temperatures and much longer time are used in Mg–Co–H system. This is one reason why the average size of Mg_2Co particles is a little larger than that of Mg_2Ni particles. The great difference of catalytic effect of Co and Ni in the preparation of metal hydrides in Mg–M–H ($M = \text{Co}$ or Ni) system and different reaction mechanisms are also possible reasons. It is obvious that Ni has a much better catalytic effect than Co in the hydrogen absorption and desorption processes. This is also one reason for the great difference in research interest between Mg–Ni–H and Mg–Co–H systems. The Mg_2CoH_5 and the Mg_2Co particles are smaller than the original Mg particles because the particles expand when heated and disintegrate into smaller ones owing to the entry of hydrogen during the absorption and desorption process. The inserted electron diffraction pattern in Fig. 2(d) confirms that the particles are from the Mg_2Co compound.

3.3. Hydrogen storage behavior

Fig. 3 shows the hydrogen absorption curves of the three samples (Mg nanoparticles, 2Mg+Co nanoparticle mixture and the obtained S7) in the first cycle at 673 K under 40 bar hydrogen atmosphere. The vertical axes in Fig. 3(a) and (b) represent the absorption reaction percent (%) and the hydrogen absorption content in the form of H/Mg expressed by the number of hydrogen atoms per Mg atom, respectively. The Mg nanoparticles absorb hydrogen in 40 bar hydrogen pressure at 673 K completely in 65 min in the first cycle [12]. This absorption rate is faster than bulk magnesium or large magnesium particles. The 2Mg+Co nanoparticle mixture sample absorbs hydrogen at a higher rate than Mg nanoparticles because of the Co catalytic effect in hydrogen absorption. But the whole hydrogen absorption process requires a longer time to finish. After 62 min of absorption measurements, we obtain S3. The hydrogen absorption process is about 83% completed. Combining the composition results of S3, we can see that reaction (2) has finished (then the reaction percent will be 80%) after 1-h absorption and the sample is in the process of reaction (3), which is thought to be a little slow compared with reaction (1). We can see that S7 (mainly Mg_2Co) absorbs hydrogen at a lower rate than the 2Mg+Co mixture sample. The absorption process is not easy to finish compared with Mg nanoparticles or 2Mg+Co mixture sample and there will always be some unreacted Mg_2Co and other impurity phases in S8.

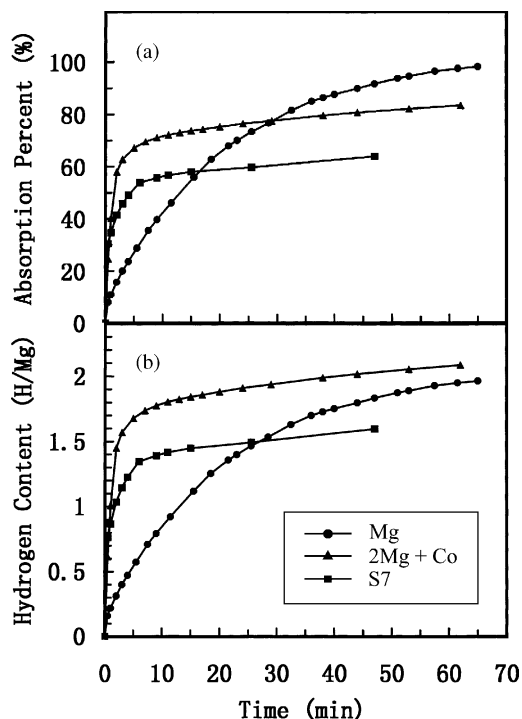


Fig. 3. Hydrogen absorption curves of the samples in the first cycle at 673 K under 40 bar hydrogen atmosphere. The vertical axis represents: (a) the absorption reaction percent (%) and (b) the hydrogen absorption content in the form of H/Mg.

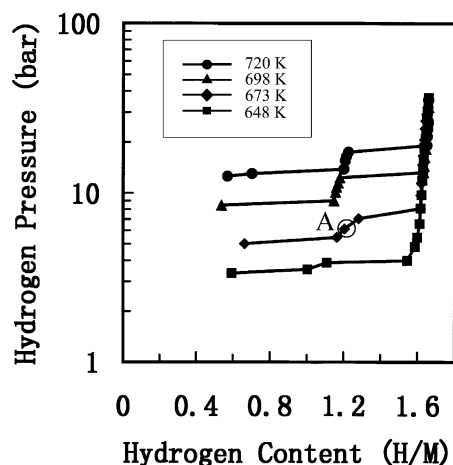


Fig. 4. Pressure–composition isotherm curves of S4 at 648, 673, 698 and 720 K.

Fig. 4 shows the desorption P – C – T curves of S4 (mainly Mg_2CoH_5) at 648, 673, 698 and 720 K. There are two equilibrium plateaux during the desorption process at each temperature. Combining the composition results of S5 (see Table 1 and dot A in Fig. 4), we can conclude that the higher plateaux and the lower ones correspond to Mg_2CoH_5 and Mg_3CoH_5 , respectively. The equilibrium plateau pressures for desorption of Mg_2CoH_5 and Mg_3CoH_5 at different temperatures are shown in Table 2 and the van't Hoff plot for

Table 2
Equilibrium plateau pressures for desorption of Mg_2CoH_5 and Mg_3CoH_5 at different temperatures

T (K)	$P_{\text{Mg}_2\text{CoH}_5}$ (bar)	$P_{\text{Mg}_3\text{CoH}_5}$ (bar)
648	3.93	3.45
673	7.59	5.24
698	12.80	8.75
720	18.31	13.45

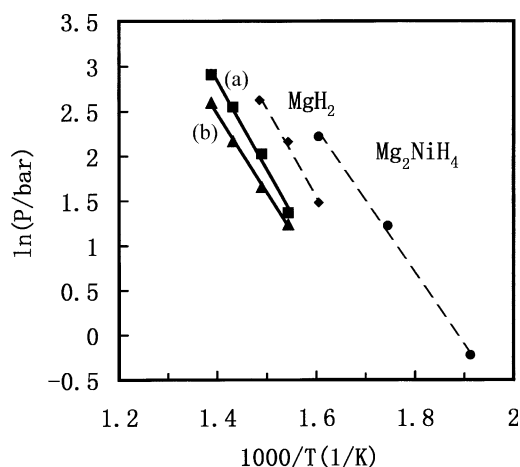


Fig. 5. Van't Hoff plot for (a) Mg_2CoH_5 , and (b) Mg_3CoH_5 and the former results of MgH_2 and Mg_2NiH_4 by our group.

Mg_2CoH_5 and Mg_3CoH_5 are shown in Fig. 5. The equilibrium plateau pressures for Mg_2CoH_5 are 3.93, 7.59, 12.80 and 18.31 bar and those for Mg_3CoH_5 are 3.45, 5.24, 8.75 and 13.45 bar at 648, 673, 698 and 720 K, respectively. The experimental van't Hoff desorption equations are $\ln(P/\text{bar}) = -9895/T + 16.70$ for Mg_2CoH_5 and $\ln(P/\text{bar}) = -8800/T + 14.80$ for Mg_3CoH_5 . The formation enthalpy (ΔH) and entropy (ΔS) are $-82.27 \text{ kJ/mol H}_2$ and $-138.8 \text{ J/K mol H}_2$ for Mg_2CoH_5 and $-73.16 \text{ kJ/mol H}_2$ and $-123.0 \text{ J/K mol H}_2$ for Mg_3CoH_5 , respectively. On desorption of P - C - T properties of Mg_2CoH_5 , there are some confusing results in the literature. Zolliker et al. found only one plateau (there are two plateaux in their P - C - T curves, but one is ascribed to MgH_2 impurity). But their resulting formation enthalpy of Mg_2CoH_5 (-86 kJ/mol H_2) agrees with ours. Chen et al. [21] also found only one plateau, but the resulting formation enthalpy (-83.2 kJ/mol H_2) and the formation entropy ($-146.7 \text{ J/K mol H}_2$) of Mg_2CoH_5 are also in good agreement with ours. Yoshida et al. [22] found two plateaux at temperatures above 671 K. Now the most accordant results with us is by the Ivanov group [10]. They found two plateaux at each temperature during the hydrogen desorption of Mg_2CoH_5 compound. They also estimated that the low-plateau hydride was probably Mg_3CoH_5 by chemical microprobe analysis. The formation enthalpy (ΔH) and entropy (ΔS) of their results

are $-79 \pm 4 \text{ kJ/mol H}_2$ and $-134 \pm 4 \text{ J/K mol H}_2$ for Mg_2CoH_5 and $-70 \pm 4 \text{ kJ/mol H}_2$ and $-118 \pm 4 \text{ J/K mol H}_2$ for Mg_3CoH_5 . In Fig. 5, we also present the former results of MgH_2 and Mg_2NiH_4 by our group. At a temperature of about 673 K, Mg_2NiH_4 compound has a higher equilibrium plateau pressure than MgH_2 , while Mg_2CoH_5 and Mg_3CoH_5 have lower equilibrium plateau pressures than MgH_2 .

4. Conclusions

Nanostructured Mg_2CoH_5 and Mg_2Co sample were successfully synthesized at 673 K in 40 bar hydrogen atmosphere from Mg and Co nanoparticles produced by HPMR method. The nanometer-scale effect plays an important role in synthesis in such convenient conditions. The average size of Mg_2CoH_5 and Mg_2Co particles is about 150 nm, which is smaller than that of Mg particles. The reason for this phenomenon is that the particles expand and disintegrate into small ones because of the entry of hydrogen. The $2\text{Mg} + \text{Co}$ nanoparticle mixture sample absorbs hydrogen at a higher rate than the Mg nanoparticles at 673 K in 40 bar hydrogen atmosphere because of the catalytic effect of Co. But it takes a longer time for $2\text{Mg} + \text{Co}$ mixture sample and Mg_2Co to finish the hydrogen absorption process than Mg nanoparticles in the first cycle at 673 K. The equilibrium plateau pressures for Mg_2CoH_5 are 3.93, 7.59, 12.80 and 18.31 bar, and those for Mg_3CoH_5 are 3.45, 5.24, 8.75 and 13.45 bar at 648, 673, 698 and 720 K, respectively. The van't Hoff desorption equations are $\ln(P/\text{bar}) = -9895/T + 16.70$ for Mg_2CoH_5 and $\ln(P/\text{bar}) = -8800/T + 14.80$ for Mg_3CoH_5 . The formation enthalpy (ΔH) and entropy (ΔS) for Mg_2CoH_5 are $-82.27 \text{ kJ/mol H}_2$ and $-138.8 \text{ J/K mol H}_2$ and those for Mg_3CoH_5 are $-73.16 \text{ kJ/mol H}_2$ and $-123.0 \text{ J/K mol H}_2$, respectively.

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