

Research Article

Thermodynamic Property Study of Nanostructured Mg-H, Mg-Ni-H, and Mg-Cu-H Systems by High Pressure DSC Method

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Mg, Ni, and Cu nanoparticles were synthesized by hydrogen plasma metal reaction method. Preparation of Mg₂Ni and Mg₂Cu alloys from these Mg, Ni, and Cu nanoparticles has been successfully achieved in convenient conditions. High pressure differential scanning calorimetry (DSC) technique in hydrogen atmosphere was applied to study the synthesis and thermodynamic properties of the hydrogen absorption/desorption processes of nanostructured Mg-H, Mg-Ni-H, and Mg-Cu-H systems. Van't Hoff equation of Mg-Ni-H system as well as formation enthalpy and entropy of Mg₂NiH₄ was obtained by high pressure DSC method. The results agree with the ones by pressure-composition isotherm (PCT) methods in our previous work and the ones in literature.

1. Introduction

Mg and Mg-based alloys are widely studied as hydrogen storage materials for the advantages such as low price, light weight, high hydrogen capacity, and high abundance of Mg in the earth's crust [1–4]. The hydrides of Mg and the common Mg-based alloys show considerable hydrogen storage content—7.6 mass% for MgH₂ and 3.6, 4.5, and 5.4 mass% for Mg₂NiH₄, Mg₂CoH₅, and Mg₂FeH₆, respectively. Recently some new hydrogen storage materials have been explored [4, 5], but Mg-based materials are still ones of the most promising hydrogen storage candidates to many researchers, especially for heat storage or stationary energy storage [3, 6], in which cases, working temperature can be above 500 K.

One serious barrier of Mg-based alloys for hydrogen storage study is synthesis of these alloys by conventional melting method because of the large difference in melting point and vaporization pressure between Mg and Ni, Co, Fe, and so forth. Ball milling/mechanical alloying method has been developed to synthesize Mg-based alloys and it is considered as one effective way to prepare nonequilibrium

alloy samples with plenty of defects and samples with grain size in nanometer scale [7]. Recently it has almost become the main preparation method by many groups to study Mg-based alloys [8–20]. However, this method faces the disadvantage of possible pollution by steel balls or air during the milling process. Another difficulty in the study of Mg-based materials is poor kinetics of these materials. For example, Mg₂Ni in micrometer scale produced by conventional melting method needs absorption/desorption temperature higher than 500 K even after several hydrogen absorption and desorption cycles under hydrogen pressure atmosphere. Common Mg metal samples in micrometer scale need much stricter conditions to absorb and desorb hydrogen. Our group and some other researchers successfully prepared nanostructured Mg-based alloy and hydride samples in convenient conditions from metal nanoparticles which were synthesized by plasma metal reaction [21–26]. These nanostructured samples show excellent hydrogen storage kinetics and properties. They can absorb and desorb hydrogen in convenient conditions without any activation process [23, 27, 28]. This work is to demonstrate that we can study the preparation process, thermodynamic properties, and reaction mechanism of

these nanostructured Mg-based materials by high pressure differential scanning calorimetry (DSC) technique under hydrogen atmosphere.

2. Experimental Details

The Mg, Ni, and Cu nanoparticles were synthesized from bulk metals by hydrogen plasma metal reaction method. Bulk Mg, Ni, and Cu metals (purity > 99.7%) were melted and vaporized by hydrogen-plasma-metal reaction in the chamber and the gaseous metals were taken to the collecting room by the circulating gas and were deposited on the filter wall, where we obtained the Mg, Ni, and Cu metal nanoparticles. To prepare Mg-Ni and Mg-Cu system alloys and hydrides, Mg and Ni (Cu) nanoparticles were weighted at a 2:1 molar ratio and mixed in acetone by an ultrasonic homogenizer. Then the mixture was dried and pressed into small pieces, from which, Mg-Ni (Mg-Cu) hydrides were synthesized in 4 MPa hydrogen atmosphere at 623 K (673 K) for 2 h (9 h) and alloys were obtained after the evacuation of the hydrides at the same temperature.

The composition and structure analysis of the samples were carried out by X-ray diffraction at an automatic Rigaku X-ray diffractometer with monochromatic Cu $K\alpha$ radiation at a scanning rate of $4^\circ/\text{min}$.

The synthesis and thermodynamic properties of Mg-H, Mg-Ni-H, and Mg-Cu-H systems were studied from DSC measurements using a NETZSCH DSC 204 HP apparatus starting from metal nanoparticles. Mg, 2Mg+Ni and 2Mg+Cu nanoparticle mixture samples with about 10 mg in weight were put into the chamber of the DSC apparatus. After closure of the system, evacuation and supply of 0.5 MPa hydrogen cycles were conducted to fresh the system. For the synthesis of Mg-Ni-H and Mg-Cu-H system, a flowing and constant hydrogen atmosphere of 4 MPa pressure was provided to the DSC chamber system. A special device is equipped in this DSC machine to keep the flowing atmosphere constant. The temperature was increased from room temperature to 823 K at a heating rate of 20 K/min. The heating and cooling processes were repeated two more cycles after the first synthesis cycle. After the production of Mg_2NiH_4 , the sample was taken through several heating and cooling cycles between 453 K and 823 K at 5, 10, and 20 K/min in various flowing and constant hydrogen pressure value (1 MPa, 2 MPa, and 4 MPa).

3. Results and Discussion

Figures 1 and 2 show the XRD curves of the metal nanoparticle samples by hydrogen plasma metal reaction method and Mg-Ni-H, Mg-Cu-H system samples prepared from these metal nanoparticles. Figure 1(a) shows the metal nanoparticle sample prepared from bulk Mg contains pure Mg phase. Mg nanoparticle sample shows hexagonal structure and the space group is $P6_3/mmc$. The size is in the range of a few hundred nm. There is a small reflection peak at 42.9° , which is due to the small amount of MgO impurity (less than 1 mass%). All of the other peaks are indexed to Mg phase. This thin layer MgO actually is very helpful to prevent the Mg particles

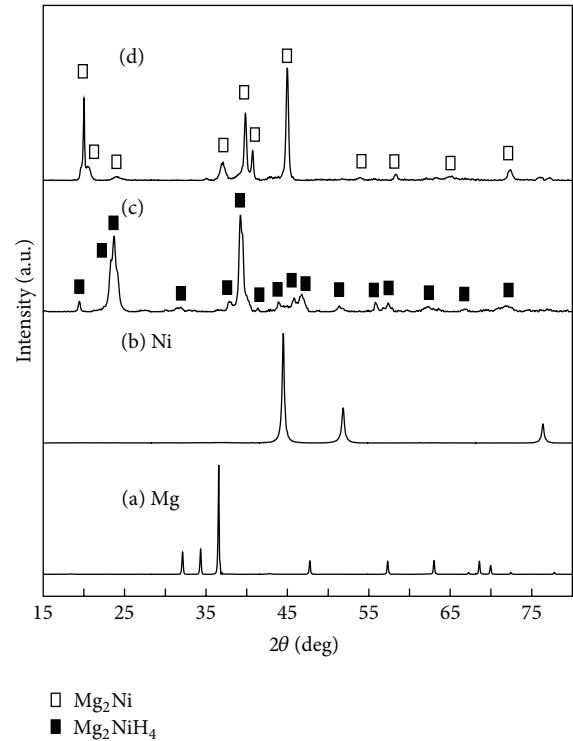


FIGURE 1: XRD patterns of (a) Mg nanoparticles, (b) Ni nanoparticles, (c) Mg_2NiH_4 sample prepared from Mg and Ni nanoparticles at 623 K in 4 MPa hydrogen for 2 hours, and (d) Mg_2Ni sample prepared after evacuation of Mg_2NiH_4 .

from further oxidation. The reflection peaks in Figure 1(b) are all ascribed to Ni nanoparticles. Ni sample shows face-centered cubic structure of $Fm\bar{3}m$ space group. The broadening of Ni peaks indicates the nanostructure of Ni samples. The particle size is about 30–50 nm. Figure 1(c) presents the Mg_2NiH_4 sample prepared from 2Mg+Ni nanoparticle mixture by sintering in 4 MPa hydrogen at 623 K for 2 h. The XRD curve is well indexed to monoclinic Mg_2NiH_4 low-temperature phase (space group: $C2/m$). After evacuation of the Mg_2NiH_4 sample, Mg_2Ni alloy (hexagonal structure, space group: $P6_222$) was obtained (Figure 1(d)). Hydrogen and nanostructure of the metal samples play important roles in the preparation of Mg_2NiH_4 and Mg_2Ni samples in convenient conditions.

Figure 2(b) indicates XRD curve of the obtained Cu nanoparticles. Only Cu phase is observed, which is face-centered cubic structure with the space group of $Fm\bar{3}m$. The Cu peaks are also broad because of the nanostructure of the Cu phase. From 2Mg+Cu nanoparticle mixture, firstly Mg-Cu-H hydride sample was obtained by sintering the mixture sample in 4 MPa hydrogen atmosphere at 673 K for 9 h and the XRD curve of the obtained hydrides sample is shown in Figure 2(c). The sample mainly consists of MgH_2 (tetragonal structure, space group: $P4_2/mnm$) and MgCu_2 (face-centered cubic structure, space group: $Fd\bar{3}m$) phases. For Mg-Cu-H system, there is no ternary hydride found in literature up to now. After the evacuation, Mg_2Cu main phase sample

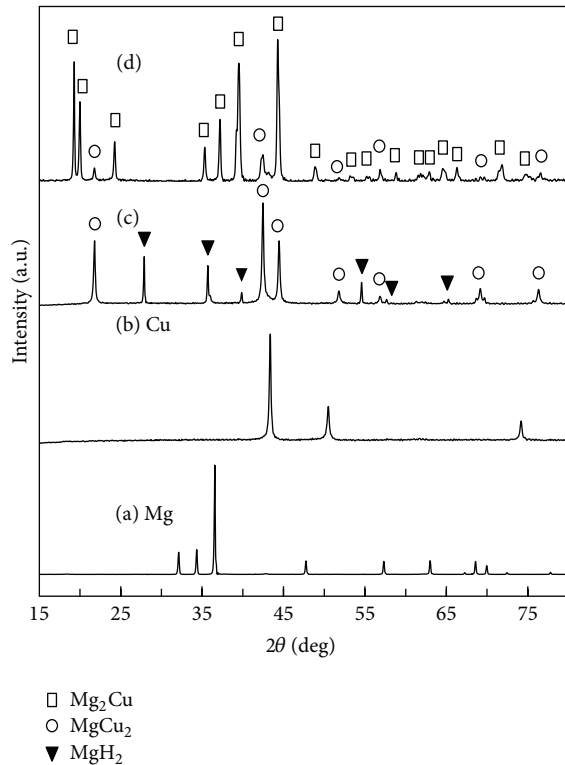


FIGURE 2: XRD patterns of (a) Mg nanoparticles, (b) Cu nanoparticles, (c) Mg-Cu-H hydride sample prepared from Mg and Cu nanoparticles at 673 K in 4 MPa hydrogen for 9 hours, and (d) Mg_2Cu sample prepared after evacuation of Mg-Cu-H hydride system.

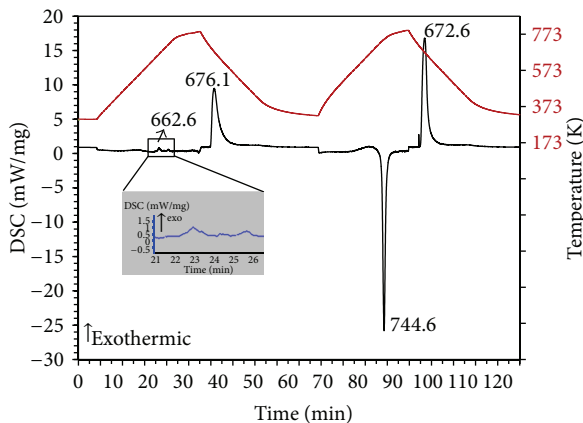


FIGURE 3: DSC curve of Mg-H system started from Mg nanoparticle sample in 4 MPa hydrogen pressure.

(orthorhombic, space group: $Fddd$) was obtained. A small amount of MgCu_2 impurity is detected.

Figure 3 shows the DSC curve of the Mg nanoparticles in an initial hydrogen pressure of 4 MPa, at a scan rate of 20 K/min. The upper dash line indicates the temperature trend and the solid line shows the DSC curve. The first peak is a small exothermic peak at 662.6 K, which is due to the

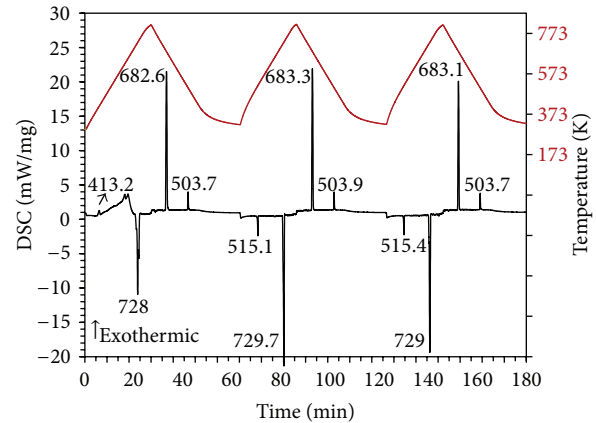
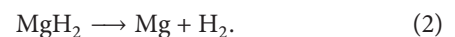
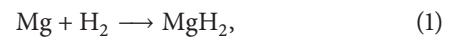


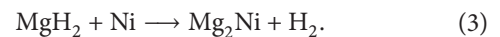
FIGURE 4: DSC curve of Mg-Ni-H system started from 2Mg+Ni nanoparticle mixture in 4 MPa hydrogen pressure.

hydrogen absorption of small amount of Mg nanoparticles. Most of the Mg begins to react with hydrogen to form MgH_2 in the first cooling cycle and shows an exothermic peak at 676.1 K. Firstly, only partial Mg sample reacts with hydrogen to form the hydride because at the beginning of the hydrogen absorption, it is difficult for hydrogen to penetrate the MgO layer on the surface of Mg nanoparticles and then enter the interior of Mg particles in very short time with heating rate of 20 K/min due to kinetic limitation. After the Mg particle surface are cracked by the entry of hydrogen, much more fresh surface occurs and makes it easier for hydrogen to enter the Mg particle interior and react with the left Mg to form MgH_2 . The reaction equations are expressed as follows:



In the second heating cycle, the hydrogenated MgH_2 desorbs hydrogen to form Mg phase and shows an endothermic peak with a peak temperature of 744.6 K (2). The formed Mg absorbs hydrogen again during the second cooling process and shows a peak temperature of 672.6 K (1).

Figure 4 presents the DSC result of starting sample-2Mg+Ni nanoparticle mixture in 4 MPa hydrogen, at a scan rate of 20 K/min. The first exothermic peak at 413.2 K is attributed to the hydrogen absorption of part of the Mg nanoparticles (1) with Ni as catalyst. The hydrogen absorption peak of Mg nanoparticles is about 250 K lowered (compared to Figure 3) when there are Ni nanoparticles as catalyst, which indicates the excellent catalytic effect of Ni nanoparticles to the hydrogen absorption of Mg phase. At about 430~450 K, there are several exothermic peaks, which are also due to hydrogen absorption of the rest Mg nanoparticles. The formed MgH_2 reacts with Ni to form Mg_2Ni and shows an endothermic peak in the first heating period at 728.0 K. The reaction is expressed as follows:



The Mg_2Ni phase absorbs hydrogen and shows an exothermic peak at 682.6 K in the first cooling cycle, which is ascribed to

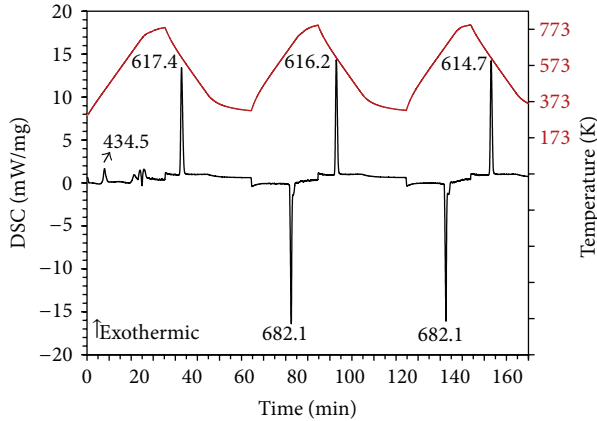
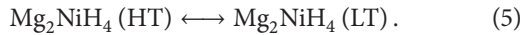


FIGURE 5: DSC curve of Mg-Cu-H system started from 2Mg+Cu nanoparticle mixture in 4 MPa hydrogen pressure.

(4). The exothermic peaks at 683.3 K in the second cooling cycle and 683.1 K in the third cycle have the same attribution:



A small exothermic peak at 503.7 K in the first cooling cycle is due to the transformation of high temperature (HT) Mg_2NiH_4 phase to low temperature one (LT) (5). The exothermic peak at 503.9 K in the second cooling cycle and the one at 503.7 K in the third cooling cycle are due to the same transformation reaction. The exothermic peak at 515.1 K in the second heating cycle and the one at 515.4 K at the third heating cycle are due to the transformation of low temperature Mg_2NiH_4 phase to high temperature one as follows:



The high and sharp peak at 729.7 K at the second heating cycle and the one at 729.0 K at the third cycle are due to desorption of Mg_2NiH_4 phase to form Mg_2Ni and hydrogen as follows:

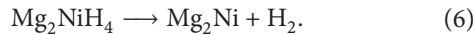


Figure 5 indicates the DSC curve of 2Mg+Cu nanoparticle mixture in 4 MPa hydrogen atmosphere. The heating and cooling rate is 20 K/min. The first exothermic peak occurs at 434.5 K, which is corresponding to the hydrogen absorption of Mg nanoparticles with Cu nanoparticles as the catalyst. This is similar to Mg-Ni-H system in Figure 4. With Cu catalyst, the hydrogenation peak temperature is lowered about 230 K. After the first exothermic peak, there are several exothermic and endothermic peaks in the temperature range of 660 K to 740 K in the first heating period. The attribution of these peaks remains unclear currently. After these peaks, the next peak at 617.4 K in the first cooling cycle could be easily defined as hydrogen absorption peak of Mg_2Cu phase according to DSC results of Mg-H system in Figure 3 and pressure-composition isotherm (PCT) results reported by us before [28]. The reactions of (1), (7), and (8) are thought to

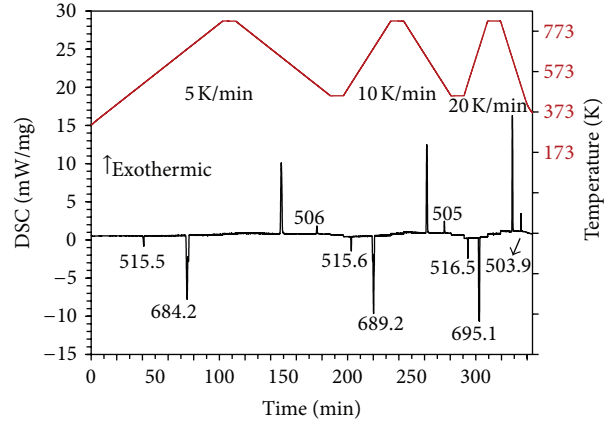
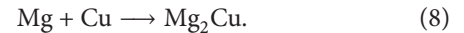


FIGURE 6: DSC curve of Mg-Ni-H system in 2 MPa hydrogen, at different scan rates started from Mg_2NiH_4 sample.

contribute to these peaks between 600 K and 740 K in the first heating process as follows:



The sharp exothermic peaks at 617.4 K, 616.2 K, and 614.7 K in the cooling period are due to the hydrogen absorption of Mg_2Cu expressed as (9), which could be easily confirmed by the XRD results after the DSC measurement. The large sharp endothermic peaks at 682.1 K in the second and third cycles are attributed to desorption of MgH_2 and MgCu_2 mixture to form Mg_2Cu and hydrogen (10). The same reaction mechanism during cycling of Mg-Cu-H system was reported by other groups [1, 29]:

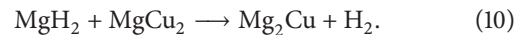
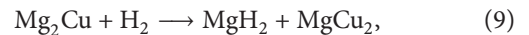


Figure 6 presents the DSC curve started from low temperature Mg_2NiH_4 phase in 2 MPa hydrogen, which is obtained from 2Mg+Ni nanoparticle mixture by DSC methods in 4 MPa hydrogen for one heating and cooling cycle. The upper dash line shows the temperature program. The middle solid line indicates the pressure change with time. During each heating and cooling cycle with different scan rates (5, 10, and 20 K/min), there are two large peaks and two small ones. These peaks have the same attribution with the ones in the second and third cycles of the DSC curve in Figure 4. They are also ascribed to (5), (6), (4), and (5) in the appearance order. From the figure, we may see that the desorption reaction of Mg_2NiH_4 to form Mg_2Ni (6) in 2 MPa hydrogen shows the peak temperatures of 684.2 K at 5 K/min, 689.2 K at 10 K/min, and 695.1 K at 20 K/min. From the pressure recording data, we obtain the real-time pressure values, which are 2.106 MPa for 684.2 K at 5 K/min, 2.106 MPa for 689.2 K at 10 K/min, and 2.107 MPa for 695.1 K at 20 K/min. These pressure, temperature and scan rate data in 2 MPa hydrogen are described in Table 1 and the values in 4 MPa and 1 MPa are

TABLE 1: Desorption temperature and pressure values from DSC measurements of Mg-Ni-H system.

Scan rate (K/min)	Desorption temperature (K)	Desorption pressure (0.1 MPa)
5	720.6	41.05
	684.2	21.06
	645.4	10.99
10	725.8	41.01
	689.2	21.06
	652.3	11.05
20	731.0	41.07
	695.1	21.07
	659.2	11.05

also included. These peaks are approximately corresponding to middle point of the desorption process. Usually we take the hydrogen equilibrium pressure of the middle point of the desorption curve during PCT measurement, and the real-time temperature of the middle point to make van't Hoff plot to obtain desorption enthalpy and entropy according to the van't Hoff equation:

$$\ln\left(\frac{P}{P^0}\right) = \frac{\Delta H}{RT} - \frac{\Delta S}{R}. \quad (11)$$

Using the data shown in Table 1, we could obtain the van't Hoff equations at different scan rates, which are given in Table 2. The van't Hoff equations vary with the scan rates because the peak temperatures for hydrogen desorption reaction from DSC technique differ at different scan rates. The higher the scan rate, the higher the temperature difference between peak temperature and real equilibrium temperature. If we want to obtain the van't Hoff equation at complete equilibrium state, we should take the DSC measurement at zero scan rate, which is impossible. However, in our case, the kinetics of the absorption and desorption reaction of nanostructured Mg-Ni-H system is superior. This means we can approach almost equilibrium state of the sorption reactions at low scan rates. After we measured the system at 5 K/min rate, we made the plot. We obtain a van't Hoff equation of $\ln(P/0.1 \text{ MPa}) = -8123/T + 14.961$ and the formation enthalpy and entropy values of -67.5 kJ/mol H_2 and $-124.4 \text{ J/(K}\cdot\text{mol H}_2)$. These results agree well with the ones from the van't Hoff equation ($\ln(P/0.1 \text{ MPa}) = -7978/T + 15.06$) and formation enthalpy and entropy values (-66.3 kJ/mol H_2 and $-125.3 \text{ J/(K}\cdot\text{mol H}_2)$, resp.) obtained by PCT technique in our previous work [23]. PCT technique is a traditional way used to make van't Hoff plot by obtaining the equilibrium pressure values of samples at various temperatures and obtain formation enthalpy and entropy values, but one whole PCT including hydrogen absorption and desorption process usually is quite time-consuming. It usually takes several days or much more depending on the hydrogen storage kinetics of the samples, measurement parameters, and equilibrium conditions. Also it has not been much noticed that the obtained equilibrium pressure values vary much with different equilibrium conditions during PCT

measurements, which could contribute to some difference in the calculated van't Hoff equation and formation enthalpy and entropy results using these plateau pressure data. By DSC technique, we could make a whole van't Hoff plot in a much more time-saving way. By comparing the results from DSC method and former PCT technique, it shows DSC method is an excellent way to obtain van't Hoff equations as well as formation enthalpy and entropy values of nanostructured hydrogen storage systems, which are with good kinetics. After we reported our method [30], Rongeat et al. reported their results about thermodynamic properties of hydrides determined by high pressure DSC method in a much different way [31]. We take the middle point of the DSC reaction peak and assume that the thermodynamics values obtained by our method are not equilibrium state while with kinetics factor, so we can compare with other people's results from desorption PCT measurements. Rongeat et al. tried to give a range of thermodynamics values of the equilibrium state between absorption measurements and desorption ones. Table 3 shows the temperature values of transformation reaction between high temperature Mg_2NiH_4 phase and low temperature one, in different hydrogen pressure values and at different scan rates. From this table, we can see that the transformation temperature from LT phase to HT phase and the one from HT phase to LT phase do not change much with the different hydrogen pressure.

4. Conclusions

The main conclusions of this work are as follows:

- (1) Nanostructured Mg-Ni-H, Mg-Cu-H hydride systems and Mg_2Ni , Mg_2Cu alloys can be obtained from Mg, Ni, and Cu nanoparticles by high hydrogen pressure DSC method.
- (2) The preparation process and hydrogen absorption and desorption properties of nanostructured Mg-H, Mg-Ni-H, and Mg-Cu-H systems were studied by DSC method. With Ni or Cu as catalyst, Mg nanoparticles absorb hydrogen at temperatures about 230–250 K lowered. Nanostructured Mg-H, Mg-Ni-H, and Mg-Cu-H systems show excellent hydrogen storage properties.
- (3) From the temperature and hydrogen pressure values obtained in DSC measurements of nanostructured Mg-Ni-H system, van't Hoff equation was obtained as $\ln(P/0.1 \text{ MPa}) = -8123/T + 14.961$ at 5 K/min scan rate. The formation enthalpy and entropy are -67.5 kJ/mol H_2 and $-124.4 \text{ J/(K}\cdot\text{mol H}_2)$. These results agree with those by PCT method.

Acknowledgments

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TABLE 2: Van't Hoff equations of Mg_2NiH_4 at different DSC scan rates.

Scan rate (K/min)	Van't Hoff equation	Formation enthalpy ($-kJ/mol H_2$)	Formation entropy $-J/(K \cdot mol H_2)$
5	$\ln(P/0.1 \text{ MPa}) = -8123/T + 14.961$	67.5	124.4
10	$\ln(P/0.1 \text{ MPa}) = -8431/T + 15.313$	70.1	127.3
20	$\ln(P/0.1 \text{ MPa}) = -8793/T + 15.728$	73.1	130.8

TABLE 3: Transformation temperatures between high temperature Mg_2NiH_4 phase and low temperature one in different hydrogen pressure values and scan rate conditions.

LT phase to HT phase			HT phase to LT phase		
Pressure (MPa)	Scan rate (K/min)	Temperature (K)	Pressure (MPa)	Scan rate (K/min)	Temperature (K)
4	20	516.6	4	20	504.7
	10	515.3		10	506.2
	5	515.0		5	507.2
2	20	516.5	2	20	503.9
	10	515.6		10	505.0
	5	515.5		5	506.0
1	20	516.5	1	20	504.1
	10	515.7		10	504.8
	5	515.6		5	505.4

in Japan and MOST of China (no. 2010CB631301 and 2011AA03A408).

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