A Comparison Study of Hydrogen Storage Thermodynamics and Kinetics of YMg₁₁Ni Alloy Prepared by Melt Spinning and Ball Milling

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Abstract Melt spinning (MS) and ball milling (BM) were employed to fabricate YMg₁₁Ni alloy, and their structures and hydrogen storage performances were examined. The results reveal that the as-spun and as-milled alloys both exhibit the nanocrystalline and amorphous structure. The as-milled alloy shows a larger hydrogen absorption capacity as compared with the as-spun alloy. More than that, the as-milled alloy exhibits lower onset hydrogen desorption temperature than the as-spun one, which are 549.8 and 560.9 K, respectively. Additionally, the as-milled alloy shows a superior hydrogen desorption property to the as-spun one. On the basis of the time needed by desorbing hydrogen of 3 wt% H₂, for the as-milled alloy, it needs 1106, 456, 343, and 180 s corresponding to hydrogen desorption temperatures of 593, 613, 633, and 653 K. However, for the as-spun alloy, the time needed is greater than 2928, 842, 356, and 197 s corresponding to the same temperatures. Hydrogen desorption activation energies of as-milled and as-spun alloys are 98.01 and 105.49 kJ/mol, respectively, which is responsible for that the as-milled alloy possesses a much faster dehydriding rate. By means of the measurement of pressure–composition–temperature (P–C–T) curves, the dehydrogenation enthalpy change of the alloys prepared by MS ($\Delta H_{\text{de}}(\text{MS})$) and BM ($\Delta H_{\text{de}}(\text{BM})$) is 81.84 and 79.46 kJ/mol, respectively, viz. $\Delta H_{\text{de}}(\text{MS}) > \Delta H_{\text{de}}(\text{BM})$.

KEY WORDS: Mg-based alloy; Ball milling; Melt spinning; Hydrogen storage kinetics; Comparison

1 Introduction

Metal hydride hydrogen storage, amidst all the hydrogen storage methods, is recognized as the preferred alternative to satisfy the requirements for vehicular application [1]. Mg and Mg-based alloys, which are considered as the great

potential hydrogen storage materials, have been extensively investigated [2–4] due to their unique advantages; for example, they have high gravimetric (7.6 wt%) and volumetric (110 kg/m³) hydrogen storage densities, good reversibility in both sorption and desorption processes, and low cost [5]. Nevertheless, some innate disadvantages of the alloys, for instance, relatively high thermal stability and bovine hydriding/dehydriding kinetics, severely restrict their practical application onboard as hydrogen storage materials. Therefore, how to further enhance the relative properties of Mg-based alloys is a huge barrier standing on the road of research. Thermodynamics and kinetics are two main parameters that affect the hydrogen storage property of alloys, which determines the practical application of hydrogen storage materials in some degree. Many works about the dual-tuning effects of thermodynamics and kinetics have been conducted [6–9]. It is proved that the structure plays a very important role in hydriding and

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dehydrogenation thermodynamics and kinetics of Mg and Mg-based alloys [10]. In particular, if the grain size of Mg-based alloys is reduced far below micrometer scale, their hydrogenation/dehydrogenation properties could be dramatically improved [11, 12]. Kumar *et al.* [13] reported that ultra-fine microstructure (sub-100 nm range) makes the desorbing hydrogen temperature of Mg_2Ni alloy decrease by 100 K, viz. from 573 to 473 K. Some techniques, for example, mechanical milling [14], rapid solidification (RS) [15], hydriding combustion synthesis [16], equal-channel angular pressing (ECAP) [17], arc plasma [18], and inert gas condensation (IGC) [19], have been put into use to compound Mg-based alloys with various kinds of components successfully.

Among the methods above, mechanical milling and melt spinning are deemed to be the fairly effective techniques, which can obtain nanocrystalline and/or amorphous alloys with elements distributed evenly. Kalinichenka *et al.* [20] found that as-spun $\text{Mg}_{85}\text{Cu}_5\text{Ni}_5\text{Y}_5$ and $\text{Mg}_{80}\text{Cu}_5\text{Ni}_5\text{Y}_{10}$ ribbons have an extraordinary amorphous structure, and these alloys are able to attain a reversible hydrogen storage density of 4.8 wt% H_2 in gravimetry. At a temperature as low as 473 K, the alloys still show a fast hydriding rate in scope of 1.5 wt% H_2 per hour. Spassov *et al.* [21] prepared $\text{Mg}_{63}\text{Ni}_{30}\text{Y}_7$ hydrogen storage alloy by rapid solidification process and obtained the maximum hydrogen absorption capacity up to approximately 3.0 wt%. Huang *et al.* [22] reported that the nanocrystalline and amorphous $(\text{Mg}_{60}\text{Ni}_{25})_{90}\text{Nd}_{10}$ alloy, which was prepared by melt spinning, yielded the highest discharge capacity of 580 mAh/g. Lass [23] reported that a rapidly solidified $\text{Mg}_{85}\text{Ni}_{10}\text{Pd}_5$ alloy exhibits a reversible hydrogen storage density of 5 wt% H_2 at the temperature of 473 K, and this temperature is near upon 100 K below the typical temperature required for Mg-based alloys. Shahi *et al.* [24] prepared $\text{MgH}_2\text{-ZrFe}_2\text{H}_x$ nanocomposites by reactive mechanical milling technique and found that the composite containing ZrFe_2 or ZrFe_2H_x brings on that the temperature of hydrogen desorption, respectively, decreases from 683 to 623 or 563 K. Hou *et al.* [25] reported the hydrogen desorption property of Mg_2NiH_4 prepared by high-energy ball milling, which utilized the multi-walled carbon nanotube combing with TiF_3 as a catalyst, and found that the hydrogen desorption temperature (T_D) and activation energy (E_a) of Mg_2NiH_4 were lowered to 503 K (516.7 K for Mg_2NiH_4) and 53.24 kJ/mol (90.13 kJ/mol for Mg_2NiH_4), respectively.

Although there are a huge number of reports about using melt spinning and ball milling technologies to prepare Mg and Mg-based alloys with amorphous and nanocrystalline structure, a general comparison of the two technologies is seldom seen. In the present work, the two technologies, viz.

melt spinning and ball milling, have been utilized to synthesize YMg_{11}Ni alloy, and a comparison of structures and hydrogen storage properties of the as-spun and as-milled YMg_{11}Ni alloys was performed.

2 Experimental

YMg_{11}Ni was prepared in a vacuum induction furnace. To protect Mg from volatilizing, the alloy was put in a helium atmosphere with a pressure of 0.04 MPa. The molten alloy was infused into a copper mold, and then, we would get a cast ingot after cooling.

YMg_{11}Ni alloy ribbons of about 40 μm in thickness and 20 mm in width were produced by a melt spinning device. The linear velocity of copper roller was used to estimate the spinning rate, and in this experiment the spinning rate was set to be 10 m/s.

A portion of the as-cast alloys was ground into particles with about 50 μm in diameter. The milling of prepared particle was processed in a planetary mill, in order to protect the particle from being oxidized; argon was filled in the containers. The samples were operated in a glove box filled with Ar. The obtained particle was put into Cr–Ni stainless steel vials with Cr–Ni stainless steel balls in a weight ratio of 35:1. Milling speed was set at 135 rpm, and total milling time was 20 h. In order to guard against overheating, milling needed to stop 10 min for refrigeration after each 60 min of working.

X-ray diffraction (XRD) (D/max/2400) is usually utilized to determine the phase constructions of the sample. The diffraction, with the experimental parameters of 160 mA, 40 kV and $10^\circ/\text{min}$, was performed with $\text{CuK}_{\alpha 1}$ radiation, using graphite as filtrator. The particle samples of as-milled alloys were observed under a high-resolution transmission electron microscope (HRTEM) (JEM-2100F, operated at 200 kV), and their crystalline states were detected by electron diffraction (ED).

Sieverts apparatus, which can control its furnace to a precision of ± 2 K automatically, was used to detect the isothermal hydriding and dehydriding kinetics and thermodynamics. The hydrogen pressure of hydrogen absorption was 3 MPa (actually, hydriding process started at this pressure), while the hydrogen desorption was conducted at a pressure of 1×10^{-4} MPa. The temperature of experiment was, respectively, 593, 613, 633, and 653 K from beginning to end. In every measurement, each cylindrical reactor loaded 300 mg samples. Non-isothermal dehydrogenation performance was investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC) (SDT-Q600) at different heating rates of 5, 10, 15 and 20 K/min.

3 Results and Discussion

3.1 Microstructure Characteristics

Phase structure and constituent characters of YMg_{11}Ni alloys prepared by both methods before and after hydrogen absorption and desorption are subjected to XRD detections; the results are exhibited in Fig. 1. The hydrogenation reaction started at 593 K and 3 MPa, and dehydrogenation reaction at 593 K and 1×10^{-4} MPa. The XRD patterns of the alloys were identified from ICDD, and the results reveal that the as-spun alloy contains two phases. Mg_{24}Y_5 and Mg_2Ni are, respectively, considered to be the major and secondary phases. It is evident that the merging and broadening of diffraction peaks caused by mechanical milling are more obvious than that caused by melt spinning, which means that the grains of as-milled alloys are refined more seriously. Moreover, the merging and broadening of diffraction peaks reflect the typical nanocrystalline and amorphous structure in both alloys. After hydrogenation, three hydrides can be found in the as-spun and as-milled YMg_{11}Ni alloys, viz. MgH_2 , Mg_2NiH_4 and YH_3 . Based on the XRD analysis, possible formation pathways of the hydrides can be inferred as follows [26]:

As Y has a bigger tendency to combine with H than Mg, the YH_2 is formed at first, after which the MgH_2 is formed. And then, YH_2 combines with H_2 and forms YH_3 . In the end, Mg_2Ni absorbs H_2 and forms Mg_2NiH_4 . The mechanism of the hydrogenation process of YMg_{11}Ni is similar to that of $\text{Mg}_{88}\text{Y}_{12}$ [26] alloy and $\text{CeH}_{2.73}\text{--MgH}_2\text{--Ni}$ composite [27].

It can also be seen that three phases appear in the dehydrogenated YMg_{11}Ni alloy, including YH_2 , Mg, and Mg_2Ni . The pathways of the dehydrogenation reactions can be inferred as follows:

The dehydrogenation process of hydrogenated YMg_{11}Ni alloy is almost opposite to the hydrogenation process, except YH_2 cannot be further decomposed. That is to say, Mg_2NiH_4 decomposes into Mg_2Ni and H_2 at first, followed by YH_3 decomposing into YH_2 and H_2 , and MgH_2 decomposes into Mg and H_2 at last. The YH_2 is undecomposable [27].

It is evident that the YH_2 phase keeps undecomposed, which is assigned to its high thermal stability. On account of the above analyses, an inference can be made that the reversible cycle of hydrogen absorption and desorption of activated alloy includes the following reactions:

Fig. 1 XRD profiles of **a** as-spun and **b** as-milled YMg_{11}Ni alloys before and after hydrogen absorption and desorption

Figure 2 illustrates the HRTEM micrographs and ED patterns of the as-spun and as-milled YMg_{11}Ni alloys before and after hydrogen absorption and desorption. Through the above information, we can easily find that the as-spun and as-milled YMg_{11}Ni alloys both possess nanocrystalline and amorphous structure (Fig. 2a, d). Additionally, the proportion of nanocrystalline in the as-milled alloy is bigger than that in the as-spun alloy, in accordance with the inference of Fig. 1, which means the more interface between the grains belongs to the as-milled alloy. Through linear intercept, we measure the average grain size, which is about 20 nm in diameter. Phase compositions of the alloys cannot be changed by melt

spinning and mechanical milling. They contain the phases Mg_{24}Y_5 and Mg_2Ni , which are also confirmed by the analysis of ED patterns. After hydrogenation, the as-spun and as-milled YMg_{11}Ni alloys both display a nanocrystalline structure (Fig. 2b, e) and the grain sizes visibly grow, suggesting that hydrogen absorption facilitates crystalline reaction. Three hydrides, MgH_2 , Mg_2NiH_4 , and YH_3 , appear in the hydrogenated as-spun and as-milled alloys, which are supported by ED patterns. The structural analysis and index of ED rings reveal that there are three phases in dehydrogenated as-spun and as-milled YMg_{11}Ni alloys (Fig. 2c, f), viz. Mg, Mg_2Ni and YH_2 . Apparently, the YH_2 maintains undecomposed in the

Fig. 2 HRTEM micrographs and SAD patterns of YMg_{11}Ni alloy at different states: **a** as-spun YMg_{11}Ni , **b** as-spun and hydrogenated YMg_{11}Ni , **c** as-spun and dehydrogenated YMg_{11}Ni , **d** as-milled YMg_{11}Ni , **e** as-milled and hydrogenated YMg_{11}Ni , **f** as-milled and dehydrogenated YMg_{11}Ni

process of hydrogen desorption, which is in line with XRD detections.

3.2 Hydrogen Absorption and Desorption Kinetics

To examine the hydrogen absorption kinetics changed by melt spinning and ball milling, the variations of hydrogen absorption capacity of the as-spun and as-milled YMg_{11}Ni alloys with hydriding reaction time are, respectively, measured at 593, 613, 633, and 653 K and 3 MPa, as exhibited in Fig. 3. It is clear that the as-spun and as-milled YMg_{11}Ni alloys absorb hydrogen at a quite high rate in its infancy, and then after quite a long time for hydriding the content of hydrogen is nearly saturated. These hydrogenation curve characteristics of the as-spun and as-milled alloys are most likely dominated by the fact that in the first few minutes a hydride layer, which is near the surface, is formed, so that hydrogen diffusing through this layer becomes the rate-limiting factor. In order to make it easier to compare, 60 s is taken as a reference of the hydrogen absorption time. Through Fig. 3, we can acquire the information that the hydrogen absorption capacity within 60 s at 593, 613, 633, and 653 K is 4.070, 4.394, 4.543, and 4.684 wt%, respectively, for the as-spun YMg_{11}Ni alloy, and 4.076, 4.399, 4.559, and 4.715 wt% for the as-milled one. It indicates that ball milling renders a more significant contribution to increase the hydrogen sorption rate of the alloys as compared with melt spinning. It is well known that the hydrogenation process of MgH_2 is dominated by three critical steps, namely (a) the process of H_2 molecules dissociating into H atoms on the surface of the alloy, (b) the diffusion of H atoms through grain boundaries, and (c) the reversible process of H atoms transforming into MgH_2 molecules. The faster hydriding rate of the as-milled alloy is most likely ascribed to the ball milling facilitating the step (b), i.e., the diffusion of H atoms through grain boundaries. Due to the decreased particle size and increased high surface-to-

volume ratio of alloy particles produced by ball milling, the distance for H atoms diffusing through the hydride is cut down dramatically, which facilitates the absorption kinetics greatly [28].

Figure 4 exhibits the temperature-programmed desorption curves of the as-spun and as-milled YMg_{11}Ni alloys in saturated hydrogen absorption state at 593 K and 3 MPa at a heating rate of 5 K/min in a closed chamber. To shun the effect of extra pressure on desorption temperature, we took every sample with the same weight for comparison. It is indicated from Fig. 4 that the as-spun and as-milled YMg_{11}Ni alloys start to release hydrogen at about 560.9 and 549.8 K with the total dehydrogenation capacities of 5.066 and 5.291 wt% H_2 by 698.4 and 699.1 K. The initiative hydrogen desorption temperature of the as-milled alloy has a reduction by 11.1 K as compared with the as-spun alloy. It suggests that the change of preparation technology affects the onset desorption temperature of MgH_2 as Pukazhselvan *et al.* [29] reported.

As illustrated in Fig. 5, to inspect the effect of changing preparation technology on hydrogen desorption kinetics of YMg_{11}Ni alloy, isothermal dehydrogenation measurements of the as-spun and as-milled YMg_{11}Ni alloys were taken at different temperatures. The isothermal dehydrogenation curves of the as-spun and as-milled alloys were, respectively, analyzed at 593, 613, 633, and 653 K. It is clear that the temperature change has a significant relationship with the hydrogen desorption kinetics of these alloys. The temperature rising evidently enhances the dehydriding rate of the alloys. It can be found by a comparison between Fig. 5a, b that the as-milled alloy shows a much faster dehydriding rate. It can be derived from Fig. 5 that the times needed by desorbing 3 wt% H_2 at 593, 613, 633, and 653 K are 2928, 842, 356, and 197 s, respectively, for the as-spun alloy, and 1106, 456, 343, and 180 s for the as-milled one. These results make clear that the dehydrogenation kinetics of YMg_{11}Ni alloy was obviously influenced by the preparation technology.

Fig. 3 Hydrogen absorption kinetic curves of **a** as-spun and **b** as-milled YMg_{11}Ni alloys at different temperatures

3.3 Hydrogen Desorption Activation Energy

In order to find out clearly the mechanism of the as-milled alloy possessing faster hydriding rate as comparing the as-spun one, hydrogen desorption activation energies of both alloys were estimated by Arrhenius and Kissinger methods. Fan *et al.* [30] considered that the activation energy (E_a) of hydrogen desorption can evaluate the dehydrogenation property very well. Hydrogen desorption kinetics is thought to have a relationship with the energy barrier for H_2 releasing from MgH_2 . Generally, activation energy is utilized to indicate the whole energy barrier for a gas–solid reaction overcoming. As to hydrogen desorption reaction, the activation energy is considered to have a relationship with the whole energy barrier of hydrogen desorption process. The hydrogen desorption reaction was performed in a nucleation and growth process. Usually, the process of nucleation and growth which occur in the period of hydrogen desorption is simulated by Johnson–Mehl–Avrami (JMA) model, described by the equation as follows [31]:

Fig. 4 Temperature-programmed desorption curves of as-spun and as-milled $YMg_{11}Ni$ alloys after hydrogen absorption at a heating rate of 5 K/min

Fig. 5 Hydrogen desorption kinetic curves of **a** as-spun and **b** as-milled $YMg_{11}Ni$ alloys at different temperatures

$$\ln[-\ln(1-\alpha)] = \eta \ln k + \eta \ln t, \quad (11)$$

where α represents the phase fraction transformed at time t , which can be recognized by a normalized hydrogen weight percentage (range from 0 to 1), k represents an effective kinetic parameter, and η stands for the Avrami exponent. JMA graphs of $\ln[-\ln(1-\alpha)]$ versus $\ln t$ at 593, 613, 633, and 653 K can be constructed by using logarithmic transformation of Eq. (11), as illustrated in Fig. 6. The JMA plots are found to be nearly linear, implying that the dehydriding reaction of the alloys follows an instantaneous nucleation followed by interface-controlled three-dimensional growth process [32]. Thus, the η and $\eta \ln k$ values at different temperatures can be derived from the slope and intercept of JMA plots, and then, the rate constant k can be easily calculated. Activation energy of the hydrogen desorption process (E_a^{de}) can be counted by Arrhenius equation as follows [33]:

$$k = A \exp(-E_a^{de}/RT), \quad (12)$$

where A means an independent temperature coefficient, T represents the absolute temperature, R stands for the universal gas constant (8.3145 J/(mol K)). The Arrhenius plots of $\ln k$ versus $1/T$ of the alloys are given in Fig. 6. Therefore, the E_a^{de} can be derived from the slopes of Arrhenius plots. The E_a^{de} values of the as-spun and as-milled $YMg_{11}Ni$ alloys are 105.49 and 98.01 kJ/mol. There is a reduction of 7.48 kJ/mol in activation energy. The E_a^{de} values of both alloys are much lower than that of pure MgH_2 (156 kJ/mol) [34], and this is deduced to be the result of the synergistic effect of YH_3/YH_2 and Mg_2NiH_4/Mg_2Ni [27].

At the same time, we also count the hydrogen desorption activation energy by Kissinger method for comparison. The Kissinger equation is given as follows [35]:

$$d[\ln(\beta/T_p^2)]/d(1/T_p) = -E_k^{de}/R, \quad (13)$$

Fig. 6 JMA graphs and Arrhenius plots of **a** as-spun and **b** as-milled YMg₁₁Ni alloys (The insets show the Arrhenius plots)

where β stands for the heating rate, E_k^{de} represents activation energy counted by Kissinger method, and T_P means the absolute temperature corresponding to the maximum desorption rate in DSC curves. Considering the calculation conditions of Kissinger method, we, respectively, utilize DSC to measure the non-isothermal hydrogen desorption reactions of YMg₁₁Ni alloys prepared by both methods, which were hydrogenated at 593 K and 3 MPa at different heating rates of 5, 10, 15, and 20 K/min. It indicates that the hydrogen desorption is corresponding to a distinct endothermic peak, and the alloys all exhibit peaks of a semblable shape, which manifests the same process of each reaction. In addition, the endothermic peak of the as-milled alloy has a tendency to lower the temperature for all heating rates, which indicates ball milling also improves the reaction rate of hydrogen desorption process. Based on the data of Fig. 7, the graphs of $\ln(\beta/T_P^2)$ versus $1/T_P$ can be built by logarithmic transforming Eq. (13), which is termed as Kissinger plots as inserted in Fig. 7. The Kissinger plots are almost linear, and thus, the activation energy E_k^{de} can be readily calculated through the slopes of Kissinger plots. By utilizing the above method, we would find the E_k^{de} values of the as-spun and as-milled alloys are

96.93 and 91.53 kJ/mol, respectively. It indicates that activation energy counted by Kissinger method has a bit difference from the one by Arrhenius method that the former is smaller than the latter. Baricco *et al.* [36] reported similar values. Therefore, whichever method is used, the as-milled alloy exhibits lower activation energy than the as-spun one. This is thought to be the result of the high-density interfacial energy between Mg phase and YH₂ or Mg₂Ni phase in the YMg₁₁Ni alloy embedded by YH₂ or Mg₂Ni nanoparticles (Fig. 2c, f), which is beneficial for cutting down the distance for H atoms diffusing through the alloys and improving the kinetics. In some other RE–Mg–Ni alloys, the decrease in activation energy caused by high-density interface required for effective catalysis has been found as well [37, 38]. The as-milled alloy has more interface than the as-spun alloy, one of the inferences of Fig. 2, and the interface can provide fast diffusion way and induce local stress for hydrogen, sequentially enhance the reactions at interface region, thus improving the hydrogenation and dehydrogenation kinetics [39]. That is why the as-milled alloy has a more excellent hydrogenation and dehydrogenation kinetics than the as-spun alloy. In view of the above results, we can draw a conclusion that the decreased hydrogen desorption activation energy led by

Fig. 7 DSC curves and Kissinger plots of **a** as-spun and **b** as-milled YMg₁₁Ni alloys at various heating rates (The insets show the Kissinger plots)

Fig. 8 P–C–T curves and van't Hoff plots of **a** as-spun and **b** as-milled YMg₁₁Ni alloys in the temperature range of 593–653 K

Table 1 Enthalpy change (ΔH) and entropy change (ΔS) of as-spun and as-milled alloys

State	ΔH_{ab} (kJ/mol)	ΔS_{ab} (J/mol/K)	ΔH_{de} (kJ/mol)	ΔS_{de} (J/mol/K)
As-spun	−78.63	−121.87	81.84	126.62
As-milled	−77.83	−118.71	79.46	120.15

ball milling is the real driving power of enhancing hydrogen desorption property.

3.4 Hydrogen Storage Thermodynamics and P–C–T Curves

In order to inspect the influence of melt spinning and ball milling for the hydrogen absorption/desorption thermodynamics of YMg₁₁Ni alloy, P–C–T curves of the alloys, respectively, recorded the information at different four temperatures of 593, 613, 633, and 653 K, as presented in Fig. 8. It indicates that the hydriding pressure plateaus (P_a) and dehydriding pressure plateaus (P_d) of the as-spun and as-milled alloys are fairly flat, and the hysteresis of the pressure plateaus between the hydriding and dehydriding ($H_f = \ln(P_a/P_d)$) is quite small (P_a and P_d are the pressure plateaus of absorption and desorption, respectively). Melt spinning and ball milling have an insignificant effect on the plateau features of P–C–T curves. Clearly, each P–C–T curve has two pressure plateaus, the lower of which corresponds to the formation and decomposition of MgH₂, and the higher plateau corresponds to that of Mg₂NiH₄. Based on the plateau pressures (P_a and P_d) in Fig. 8, we can calculate the thermodynamic parameters, viz. enthalpy change (ΔH) and entropy change (ΔS) of the hydriding/dehydriding reaction, by van't Hoff equation [40]:

$$\ln(P_{H_2}/P_0) = \Delta H/(RT) - \Delta S/R, \quad (14)$$

where P_{H_2} is the equilibrium hydrogen gas pressure (for having two pressure plateaus, here, we take the pressure corresponding to MgH₂ as equilibrium hydrogen gas pressure), P_0 represents the standard atmospheric pressure. The van't Hoff graphs of $\ln(P_{H_2}/P_0)$ versus $1/T$ for the as-

spun and as-milled YMg₁₁Ni alloys can be plotted by using logarithmic transformation of Eq. (14), as inserted in Fig. 8. Thus, it is easy to calculate the thermodynamic parameters from the slopes and intercepts of van't Hoff plots, including enthalpy change of hydrogen absorption (ΔH_{ab}) and desorption (ΔH_{de}), and entropy change of hydrogen absorption (ΔS_{ab}) and desorption (ΔS_{de}), as Table 1 lists. It indicates that for the alloy, ball milling renders a slight improvement on hydrogen storage thermodynamics. During ball milling, the grain size can be minished more dramatically than melt spinning (Fig. 1). When the grain size decreases to small enough, the enthalpy data will be changed theoretically according to Lass [20], because of the new introduced capillarity. The slight improvement on hydrogen storage thermodynamics led by BM compared with MS means a little more ultra-fine grains appearing during ball milling.

4 Conclusions

1. The preparation technologies, including melt spinning and ball milling, engender an insignificant effect on the thermodynamic parameters (ΔH and ΔS) of YMg₁₁Ni alloy. Ball milling visibly impairs the stability of alloy hydride compared with melt spinning. The initial hydrogen desorption temperatures of the hydrogenated as-spun and as-milled YMg₁₁Ni alloys are 560.9 and 549.8 K, respectively.
2. Comparing melt spinning and ball milling, we could find the latter enhances the hydrogen absorption and desorption kinetics more obviously, which is ascribed

to the diminished particle size and decreased hydrogen desorption activation energy.

3. The hydrogen desorption activation energies of the as-spun and as-milled YMg_{11}Ni alloys are counted by Arrhenius and Kissinger methods. By analyzing the results of experiment, we could draw a conclusion that ball milling has a more obvious effect on reducing hydrogen desorption activation energy and that may explain the enhanced hydrogen desorption kinetics of the as-milled alloys.

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