The high dehydrogenation kinetics are the results of low activation energy combined with amorphous and nanocrystalline structure.
Dehydrogenation behavior and microstructure evolution of hydrogenated Magnesium-Nickel-Yttrium melt-spun ribbons

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Abstract

This paper reports porous Mg$_{67}$Ni$_{33-x}$Y$_x$ ($x = 0, 1, 3, 6$) ribbons which are prepared by a melt spinning method. The dehydrogenation behaviors, including the thermal decomposition process, dehydrogenation capacities, percent and kinetics, are investigated in a temperature range of 523-623 K. The microstructure evolution during dehydrogenation process of metal melt-spun ribbons is discussed in the aspect of the microstructures of hydrogenated and dehydrogenated ribbons. It is considered that the porous structure in the as-prepared ribbons accelerates the diffusion of hydrogen gas and atoms, and increases dehydrogenation nucleation locations and decreases the diffusion distance. Additionally, the addition of Y elements and melt-spinning decreases the activation energy of dehydrogenation. Low activation energy and refined microstructure play a dominant role in decreasing the dehydrogenation temperature and increasing the kinetics of Mg-based metal melt-spun ribbons.

Keywords: hydrogen storage; rapid solidification; nanocrystalline; rare earth; activation energy
1. Introduction

Magnesium-based alloys are considered as an promising medium of hydrogen storage for on-board vehicle and stationary applications on solving environment and energy issues, due to the high theoretical storage capacity (e.g. Mg 7.6 wt. %), light weight and abundant resources. However, the magnesium-based alloys have a high stability of the hydrides and low hydrogen atoms diffusion rate, which arouse the high dehydrogenation temperature and low hydrogen desorption kinetics, and limit it in industrial applications.\(^1\)

A great many of efforts have been devoted to improving the dehydrogenation properties of the Mg-based alloys from two aspects, element doping and microstructure modification. The work has proved that the addition of transition metal elements,\(^2,3\) rare metal elements\(^4,5\) and catalysts\(^6,7\) into Mg-based alloys decreases the stability of hydrides and increases the dehydrogenation kinetics.\(^8\) However, the excellent kinetics caused by the addition of transition metal elements are at the expense of low dehydrogenation capacities. It has been found that rare earth (RE) elements not only accelerate the dehydrogenation kinetics, but also enhance the dehydrogenation capacity comparing with transition metal elements by substituting B side elements of A\(_2\)B-type Mg-based alloy, and decrease the hydrogen desorption temperature.\(^9\) By adding rare earth elements, the high activation of rare earth elements has catalysis on the decomposition of hydrogen molecules on the surface of alloy particles.\(^10\) During the dehydrogenation process, the compounds and RE hydrides could be formed in the alloys and these products proven to provide positive catalysis on the formation and decomposition of other hydrides.\(^11\) Especially, the yttrium (Y) is lighter than other RE elements, it is favorable to increase gaseous hydrogen absorption/desorption capacities per unit mass. Additionally, the strain and defects, which are induced by the formation and decomposition of YH\(_2\)/YH\(_3\), are proved to facilitate the hydrogen absorption and desorption.\(^10\) The addition of elements and catalysts can significantly improve the
hydrogenation/dehydrogenation rates, however, these methods still cannot solve the problems of slow dehydrogenation kinetics well. The microstructure is closely related to the thermodynamic and kinetics of hydrogenation/dehydrogenation. The diffusion of hydrogen atoms in alloys and hydrides is an important factor to the hydrogen desorption kinetics. The refined grain size to nanoscale and amorphous structure can significantly enhance the hydrogen absorption/desorption kinetics and hydrogen storage capacity since the refined grain generates a large amount of interfaces along which hydrogen atoms can diffuse more easily. For microstructure modification, ball milling and melt spinning are proved to be powerful techniques to produce amorphous and nanocrystalline Mg$_2$Ni alloys. However, ball milling is still limited to some unavoidable shortcomings: contamination of metal powders by milling equipment and oxygen even in argon atmosphere, small scale production and requires relatively high cost for special safe handling the powder such as heat-transfer and pipe blockage. In addition, the growth of ball milled particle occurs at high reaction temperature and deteriorates the kinetic properties. On the contrary, the microstructure stability of melt spun ribbons is higher than that of ball milled particles during the hydrogenation and dehydrogenation cycles. Generally speaking, the amorphous and nanocrystalline Mg-based alloys prepared by melt-spun have faster hydrogen absorption and desorption kinetics. Melt spinning has been proven as an effective method to reduce the grain size and possesses attractive hydrogenation/dehydrogenation properties. In addition to the enhanced diffusivity of hydrogen atoms, the diffusion distance is also decreased by melt spinning. The melt-spun ribbons can absorb and release hydrogen from two sides, therefore the ribbons can be hydrogenated completely with the thickness less than 50 µm. In addition, increased porosity in metals significantly increases the diffusion of gas. The dehydrogenation property is closely related to the microstructure, the microstructure evolution during dehydrogenation process is necessary to analyze the dehydrogenation mechanism of melt spun ribbons.
The two important factors on hydrogen desorption kinetics are dehydrogenation energy barrier of hydrides and the diffusion of hydrogen atoms. The addition of RE elements facilitates the glass forming of Mg$_2$Ni-based alloys. The melt spinning technique combined with the addition of Y element into Mg$_2$Ni alloys is employed in this work to decrease the dehydrogenation energy barrier of hydrides and facilitate the diffusion of hydrogen atoms. Special attentions have been paid to the microstructure evolution and phase transformation of Y-doped Mg-based melt-spun ribbons during dehydrogenation process. The activation energy of the dehydrogenation reaction is calculated by the Kissinger method. In addition, the effect of temperature on dehydrogenation kinetics is also emphasized and the corresponding influencing factors are discussed. The corresponding dehydrogenation mechanism of Mg-Ni-Y melt-spun ribbons is proposed in this work.

2. Experimental

Mg-based hydrogen storage alloys with the composition of Mg$_{67}$Ni$_{33-x}$Y$_x$ ($x = 0, 1, 3, 6$ at. %) were melted under the protection of covering flux in a resistance furnace. The alloys were re-melted and spun on a single copper roller with linear velocity 40 $\text{m s}^{-1}$ in an argon atmosphere of 500 mbar. The melt-spun ribbons were about 50 $\mu$m in thickness, 5 mm in width and 10-30 mm in length. The ribbons which are prepared by melt-spinning technique were directly hydrogenated in an automatic Sieverts apparatus (PCT Pro2000) under initial hydrogen pressure of 30 bar at two temperatures of 523 and 623 K for 4 h. The dehydrogenation kinetics were measured under initial vacuum at corresponding hydrogenation temperature for 1 h. Before hydrogenation/dehydrogenation measurements, all the alloy ribbons were activated by three continuous hydrogenation/dehydrogenation cycles maintaining an initial hydrogen pressure of 30 bar at 10 h for hydrogenation and vacuuming 1 h for dehydrogenation. The metallographic samples were prepared without any etching reagent even water. The phase composition and microstructure of the hydrogenated ribbons were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM, TESCAN, MIR A3 XMU) and
Transition Electron Microscope (TEM, TECNAI, F30 G²). The phase transformations during dehydrogenation of the hydrogenated ribbons were analyzed by Differential Scanning Calorimeter (DSC, NETZSCH, STA449C) at various heating rate of 5, 10, 15 and 20 K/min from ambient temperature to 723 K in an argon atmosphere.

3. Results and discussion

3.1 Phase analysis of hydrogenated ribbons

The XRD patterns of the hydrogenated Mg₆₇Ni₃₃ₓYₓ (x = 0, 1, 3, 6) melt-spun ribbons are shown in Fig. 1a. The dominant phase of the hydrogenated Mg₆₇Ni₃₃ₓYₓ (x = 0, 1, 3, 6) melt-spun ribbons is monoclinic Mg₂NiH₄. Bragg peaks of Mg₂NiH₀.₃ and MgH₂ are also observed in the XRD patterns. In addition, several Bragg peaks of MgYNi₄, YH₂, YH₃ and cubic structure Mg₂NiH₄ phases are observed in XRD pattern of the hydrogenated ribbon with x = 6. The intensity (counts) of Bragg peaks of MgH₂ phase (~ 27.9°) increases from 599 to 2375 with the increasing Y content in the hydrogenated Mg₆₇Ni₃₃ₓYₓ (x = 0, 1, 3, 6) melt-spun ribbons. It indicates that the phase content of MgH₂ increases with the increase of Y content, which coincides with the content of reactant α-Mg phase in melt-spun ribbons.²⁵ On the contrary, the phase content of Mg₂NiH₀.₃ decreases with the increase of Y content, which can be seen from the decreased intensities of Bragg peaks from Mg₂NiH₀.₃ (about 21, 37 and 47°). Mg₂NiH₀.₃ is a transitional phase of Mg₂Ni-Mg₂NiH₄ system. The addition of Y is beneficial to decrease the content of transitional phase Mg₂NiH₀.₃ by facilitating the transformation of Mg₂NiH₀.₃ to Mg₂NiH₄. The hydride of MgYNi₄ is not observed in the XRD patterns of the hydrogenated melt-spun ribbons because the MgYNi₄ absorbs hydrogen reversibly at room temperature,²⁶ and almost all of the hydrogen is released under 500 K.²⁷ The formation of hydride YH₂, as the catalyst, facilitates the forming of Mg₂NiH₀.₃ and MgH₂ during hydrogenation process.¹¹ Then the Mg₂NiH₀.₃ and YH₂ are completely hydrogenated to Mg₂NiH₄ and YH₃, respectively. The strain and defects induced by YH₂/YH₃ are believed to facilitate the hydrogenation/dehydrogenation process.¹¹
Fig. 1b shows the XRD patterns of the dehydrogenated Mg$_{67}$Ni$_{33}$$_{x}$Y$_{x}$ ($x = 0, 1, 3, 6$) ribbons. The dominant phase of dehydrogenated Mg$_{67}$Ni$_{33}$$_{x}$Y$_{x}$ ribbons is Mg$_2$Ni. The MgNi$_2$, which is eliminated by the melt-spun technique, is separated out from the dehydrogenated ribbons after 4 hydrogenation/dehydrogenation cycles. The Bragg peak intensity of MgNi$_2$ decreases with the increase of Y in the dehydrogenated ribbons. The Bragg peaks of Mg ($\sim 43.3^\circ$) and MgYNi$_4$ ($\sim 42.7^\circ$) are in the dehydrogenated Mg$_{67}$Ni$_{33}$$_{x}$Y$_{x}$ ($x = 1, 3, 6$) ribbons, their intensities increase with the increasing Y in the dehydrogenated ribbons. The YH$_2$, which is an incomplete dehydrogenated product of YH$_3$, also appears in the Bragg peaks of dehydrogenated Mg$_{67}$Ni$_{33}$$_{x}$Y$_{x}$ ribbons with $x = 6$. The phases of dehydrogenated ribbons are similar with those of the melt-spun ribbons except for the addition of MgNi$_2$ and YH$_2$ after 4 hydrogenation/dehydrogenation cycles.

Fig. 1. The XRD patterns of the (a) hydrogenated and (b) dehydrogenated Mg$_{67}$Ni$_{33}$$_{x}$Y$_{x}$ ($x = 0, 1, 3, 6$) melt-spun ribbons.
From comparing the phase structures of the hydrogenated and dehydrogenated samples, the phase transformations contain $\text{Mg}_2\text{NiH}_4$ to $\text{Mg}_2\text{Ni}$, $\text{Mg}_2\text{NiH}_{0.3}$ to $\text{Mg}_2\text{Ni}$, $\text{MgH}_2$ to Mg and $\text{YH}_3$ to $\text{YH}_2$. The $\text{MgYNi}_4$ phase appears both in hydrogenated and dehydrogenated samples, but the hydride of $\text{MgYNi}_4$ is not observed. The hydride of $\text{MgYNi}_4$ is dehydrogenated in the experimental condition probably. In addition, trace $\text{MgNi}_2$ phase precipitates out in hydrogenation/dehydrogenation cycles. The broadening of XRD patterns indicates that amorphous/nanocrystalline are included in the hydrogenated and dehydrogenated ribbons.

3.2 Microstructures of hydrogenated ribbons

The crystallite sizes of ribbons increase from 5 nm to 150 nm with addition of Y content in the melt-spun $\text{Mg}_{67}\text{Ni}_{33-x}\text{Y}_x$ ($x = 1, 3, 6$) ribbons. Fig. 2 shows the high resolution image of hydrogenated ribbons, the corresponding Selected Area Electron Diffraction (SAED) pattern and Electron Energy-Loss Spectroscopy (EELS) hydrogen mapping. The ribbons contain amorphous and nanocrystalline as shown in Fig. 2a, which is consistent with the results of XRD. The circled area is amorphous and the straight-line portion is nanocrystalline. In addition, the continuous rings with scattered diffraction points of SAED pattern also indicate that the microstructures of ribbons are amorphous and nanocrystalline. Nanocrystalline hydrides enhance the hydrogenation kinetics. The SAED pattern shows that the ribbons are polycrystalline in an electron beam diameter. The major phase $\text{Mg}_2\text{NiH}_4$ is observed in the hydrogenated ribbons in the polycrystalline SAED rings. It has been proven that the amorphous and nanocrystalline can provide passageways for the diffusion of hydrogen atoms. The grains of the hydrogenated ribbons are refined for the effect of melt-spun. The amorphous and nanocrystalline by melt-spun can shorten the diffusion distance and enhance the diffusivity of hydrogen.

The High Resolution Transmission Electron Microscopy (HRTEM) image and the corresponding Fast Fourier Transform (FFT) pattern of the hydrogenated $\text{Mg}_{67}\text{Ni}_{33-x}\text{Y}_x$ ($x = 3$) ribbon are shown in Fig. 2b. The amorphous structure and nanocrystalline are observed in the
HRTEM image. The FFT pattern is an amorphous ring with slight scattered diffraction points. Fig. 2c shows the HRTEM image of the hydrogenated $\text{Mg}_{67}\text{Ni}_{33-x}Y_x$ ($x = 6$) ribbons. The interplanar spacing and Miller indices of $\text{Mg}_2\text{NiH}_4$ are marked in the HRTEM image and SAED pattern. A lot of stacking faults are observed in the HRTEM image. Crystal defects are induced by hydrogen absorption/desorption in $\text{Mg}_2\text{Ni}$ and other hydrogen storage alloys. It has been reported that the stacking faults are beneficial to the nucleation of hydrides and lead to lower hydrogen desorption temperature and better kinetics. Comparing with the ribbons with $x = 1$ and 3, the hydrogenated ribbons with $x = 6$ contain more crystalline structures as shown in Fig 2c. Plenty of amorphous structures are observed in the melt-spun ribbons of $x = 6$ before hydrogenation. The crystallization of amorphous structure is occurred in hydrogenation process. In addition, stacking faults are formed in the crystallization process. It has been reported that changing the structure of the $\text{Mg}_2\text{Ni}$ alloy from polycrystalline to nanocrystalline results in a drop of about 100 K in absorbing/desorbing temperature. The amorphous alloy exhibits faster hydrogenation kinetics than the crystallized alloy with the same composition due to the faster hydrogen diffusion in the amorphous phase. Amorphous and nanocrystalline is helpful to the hydrogenation/dehydrogenation. In order to analyze the distribution of hydrides, the EELS hydrogen mapping is characterized as shown in Fig. 2d. The white portion is the area including hydrogen atoms. The dark particle surface gives the evidence that partial hydrogen atoms release from the particle surface under the high vacuum of the TEM and the effect of electron beam. The hydrogen desorption process has been clearly seen in the EELS maps at $\sim 400^\circ\text{C}$, but the Mg-based hydrides are rather stable at room temperature. The SAED pattern shows that the ribbons have been hydrogenated and the dominant hydride can be ascribed to $\text{Mg}_2\text{NiH}_4$. 
3.3 Microstructure evolution during dehydrogenation

The dehydrogenation process of ball milled particles has been described by Tanniru et al.\textsuperscript{34} However, the dehydrogenation process of melt-spun ribbon has not been described. In order to analyze the dehydrogenation process, the microstructures of hydrogenated and dehydrogenated melt-spun ribbons are analyzed in this work as shown in Fig. 3. Plenty connected pores, which have been observed in the microstructure of melt-spun ribbons,\textsuperscript{25} are also observed in the microstructure of hydrogenated and dehydrogenated ribbons after 4
hydrogenation/dehydrogenation cycles. Owing to the insulativity and lower z-contrast (atomic number) of the hydride, the hydride phase appears darker than the metal phase in the BSE mode. The areas around the pores are preferentially hydrogenated as shown in Fig. 3a.

The process of hydrogen desorption is an inverse process of the absorption. The areas around the pores in melt spun ribbons are similar to the surface of ball milled particles. The areas around the pores are the preferential position of dehydrogenation. The cracks can be observed in the dehydrogenated ribbons as shown in Fig. 3b. The hydrogen absorption and desorption of alloys result in the expansion and contraction of crystal lattice during the hydrogenation/dehydrogenation cycles, inducing stress in the grain. The hydrogenation/dehydrogenation cycles increase the brittleness of the ribbons, but seriously pulverization have not happened. The melt spun ribbons are distorted during hydrogenation/dehydrogenation cycles and the distortion counteracts partial distortion energy. Plenty amorphous and nanocrystalline in the melt-spun ribbons provide more diffusion paths for hydrogen atoms. The grain size reduced to nanoscale decreases the diffusion distance. The porous surface structure increases the hydrogen absorption rate. Hydrogen diffusion through the bulk metal (hydride) phase is usually quite slow and often rate-limiting. Hydrogen diffusion in gaseous phase is fast greater than that in bulk metal phase. It has been reported that fast hydrogen diffusion through or along the porous carbon phase benefit the kinetics of hydrogen release and uptake. The pores in the melt-spun ribbons provide plenty of surfaces, increasing dehydrogenation nucleation location and decreasing the diffusion distances. In addition, the released hydrogen gas can be exhausted from the ribbons by the connected pores, further improving the hydrogen desorption kinetics. The areas around the pores are the preferential position for hydrogenation/dehydrogenation.
Fig. 3. The SEM/BSE images of (a) hydrogenated and (b) dehydrogenated melt-spun ribbons.

3.4 Thermal decomposition behavior of hydrogenated ribbons

Fig. 4a shows the dehydrogenation DSC curves and the corresponding first derivative curves (DDSC) of hydrogenated Mg$_{67}$Ni$_{33-x}$Y$_x$ ($x = 0, 1, 3, 6$) melt-spun ribbons at heating rate of 10 K/min. The obvious endothermic peak around 520–560 K observed in each DSC curve can be ascribed to the dehydrogenation peak of the dominant Mg$_2$NiH$_4$ phase. The dehydrogenation phases are Mg$_2$NiH$_4$, Mg$_2$NiH$_{0.3}$, MgH$_2$ and YH$_3$ from the phase analysis. The dehydrogenation peak of the intermediate hydride Mg$_2$NiH$_{0.3}$ phase overlaps Mg$_2$NiH$_4$. The dehydrogenation temperature of MgH$_2$ is higher than that of Mg$_2$NiH$_4$, the endothermic peak of MgH$_2$ powder is about 664 K, but it is still over 593 K in the Mg$_{67}$Ni$_{10}$Y$_{10}$ alloy with the addition of Ni and Y. The trace endothermic peaks of MgH$_2$ in Fig. 4a are about 600–660 K for the minor content of MgH$_2$. It has been reported that the desorption temperature of YH$_3$ into YH$_2$ in vacuum starts at 443 K and the peak temperature is 533 K. The endothermic peak of YH$_3$ to YH$_2$ overlaps that of Mg$_2$NiH$_4$ in the Mg$_{67}$Ni$_{33-x}$Y$_x$ ribbon with $x = 6$. The main endothermic peak of Mg$_2$NiH$_4$ is not symmetric, peaks overlap on the main endothermic peak as can be seen in the DDSC curve. The decomposition of Mg$_2$NiH$_4$ is divided into two steps, which are dehydrogenation of Mg$_2$NiH$_4$ to Mg$_2$NiH$_{0.3}$ and dehydrogenation of Mg$_2$NiH$_{0.3}$ to Mg$_2$Ni. Therefore, the main dehydrogenation peaks contain overlapping peaks. The area under the peaks reveals the heat of the absorption of ribbons per unit mass. The heat of the absorption of ribbon with $x = 0$ exceeds 1700 J/g, and it
is below 1300 J/g with \( x = 1, 3 \) and 6. The addition of \( Y \) decreases the heat of the absorption of ribbons per unit mass in dehydrogenation process.

It is obvious that the peak dehydrogenation temperature (\( \sim 525 K \)) of the melt-spun ribbon with \( x = 1 \) is lower compared with that of the melt-spun ribbons with \( x = 0, 3 \) and 6 (\( \sim 542, \sim 539 \) and \( \sim 554 \) K, respectively) in Fig. 4a. In order to analyze the activation energy of the dehydrogenation reaction of \( \text{Mg}_2\text{NiH}_4 \), the dehydrogenation DSC curves of the hydrogenated \( \text{Mg}_{0.7}\text{Ni}_{3.3-x}\text{Y}_x \quad (x = 0, 1, 3, 6) \) melt-spun ribbons at heating rates of 5, 10, 15 and 20 K/min are measured and the DSC curves of \( x = 1 \) ribbons are shown in Fig. 4b. The corresponding dominated dehydrogenation peak temperatures of \( \text{Mg}_{0.7}\text{Ni}_{3.3-x}\text{Y}_x \quad (x = 0, 1, 3, 6) \) melt-spun ribbons are summarized in Table 1. The Arrhenius equation, \( k = A \exp\left(-\frac{E_a}{RT}\right) \), indicates that the lower activation energy \( E_a \) is related to faster reaction rate \( k \) and lower temperature \( T \).

The apparent activation energy for dehydrogenation of dominate phase \( \text{Mg}_2\text{NiH}_4 \) in the hydrogenated \( \text{Mg}_{0.7}\text{Ni}_{3.3-x}\text{Y}_x \quad (x = 0, 1, 3, 6) \) ribbons is calculated based on the dehydrogenation peak temperatures in Table 1 using the Kissinger equation (Equation 1).

\[
\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{A_k R}{E_k}\right) - \frac{E_k}{RT_p}
\]

(1)

Where \( \beta \) is the heating rate, \( T_p \) is the peak temperature, \( A_k \) is the preexponential factor, \( E_k \) is the dehydrogenation activation energy, \( R \) is the gas constant (8.3145 J (K mol\(^{-1}\)). \( \ln(\beta/T_p^2) \) and \( 1/T_p \) are linear correlation. Fitting curves of the hydrogenated \( \text{Mg}_{0.7}\text{Ni}_{3.3-x}\text{Y}_x \quad (x = 0, 1, 3, 6) \) melt-spun ribbons by the Kissinger method present a good linear relation between \( \ln(\beta/T_p^2) \) and \( 1/T_p \) with a slop of \( -E_k/R \), as shown in Fig. 5a. The activation energy \( E_k \) of the \( \text{Mg}_{0.7}\text{Ni}_{3.3-x}\text{Y}_x \quad (x = 0, 1, 3, 6) \) ribbons in the dehydrogenation can be summarized as 102, 73, 98 and 80 kJ/mol by Kissinger equation, respectively. The \( E_k \) of melt-spun ribbons with \( x = 0 \) is 102 kJ/mol, which is closed to the \( \text{Mg}_2\text{NiH}_4 \). The trend line of activation energy of the \( \text{Mg}_{0.7}\text{Ni}_{3.3-x}\text{Y}_x \quad (x = 0, 1, 3, 6) \) ribbons is shown in Fig. 5b. The dehydrogenation activation energy of the ribbons with \( x = 1, 3, 6 \) is lower than that of the hydrogenated ribbon with \( x = 0 \) with the
addition of Y. The hydrogenated melt-spun ribbon with \( x = 1 \) possesses the lowest activation energy of the dehydrogenation reaction among experimental alloys. The small quantity addition of Y element and refinement of the particles and grains decrease the apparent activation energy for hydrogen desorption by shortening the diffusion distance and enhancing the diffusivity with the increase of the micro strain and lattice distortion.\(^{44}\) YH\(_2\) and YH\(_3\) are generated in the Mg-based alloys in hydrogenation and dehydrogenation processes. Fine YH\(_2\)/YH\(_3\) particles provide large amount of active sites and paths to enhance the H atom diffusion along abundant phase boundaries and hydride phases.\(^{45}\) The refined grain size of alloys, multiphase structure and YH\(_2\)/YH\(_3\) decrease the activation energy during dehydrogenation.

Table 1. The dehydrogenation peak temperatures of the hydrogenated Mg\(_{67}\)Ni\(_{33}\)\(_x\)Y\(_x\) (\( x = 0, 1, 3, 6 \)) melt-spun ribbons at heating rates of 5, 10, 15 and 20 K/min.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Dehydrogenation peak temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(<em>{67})Ni(</em>{33})(_x)Y(_x)</td>
<td>5 K/min</td>
</tr>
<tr>
<td>( x = 0 )</td>
<td>527</td>
</tr>
<tr>
<td>( x = 1 )</td>
<td>507</td>
</tr>
<tr>
<td>( x = 3 )</td>
<td>526</td>
</tr>
<tr>
<td>( x = 6 )</td>
<td>538</td>
</tr>
</tbody>
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\(^{44}\)\(^{45}\)
Fig. 4. Dehydrogenation DSC and corresponding first derivative curves of the hydrogenated Mg$_{67}$Ni$_{33-x}$Y$_x$ ($x = 0, 1, 3, 6$) melt-spun ribbons. a) heating rate of 10 K/min in Mg$_{67}$Ni$_{33-x}$Y$_x$ ($x = 0, 1, 3, 6$) melt-spun ribbons, b) heating rates of 5, 10, 15 and 20 K/min in $x = 1$ ribbons.

Fig. 5. Fitted Kissinger curves and corresponding dehydrogenation activation energy curves of the hydrogenated Mg$_{67}$Ni$_{33-x}$Y$_x$ ($x = 0, 1, 3, 6$) ribbons. a) fitted Kissinger curves, b) the activation energy curves of dehydrogenation reaction

3.5 Dehydrogenation kinetics

The activation energy is related to the reaction temperature as well as the reaction kinetics. The hydrogen desorption capacities of the Mg$_{67}$Ni$_{33-x}$Y$_x$ ($x = 0, 1, 3, 6$) ribbons detected at 523 and 623 K are shown in Fig. 6. The hydrogen desorption capacities of all the ribbons added with Y are higher than Mg$_{67}$Ni$_{33-x}$Y$_x$ ($x = 0$) ribbons at 523, 573 and 623K. The addition of Y decreases the activation energy of the dehydrogenation reaction and increases the hydrogen desorption capacity corresponding with Mg$_{67}$Ni$_{33-x}$Y$_x$ ($x = 0$) ribbons. The Mg$_{67}$Ni$_{33-x}$Y$_x$ ribbons are not dehydrogenated completely at the same hydrogenation temperature from the dehydrogenation percent in Fig. 6. It can be explained that partial hydrides (such as YH$_2$) do not release hydrogen at the temperature. In addition, the hydrogen desorption is related to the hydrogen pressure as well as the temperature. The hydrogen pressure increases with the hydrogen desorption during the dehydrogenation process, and the partial hydrogen dissolved in the alloys is not released under the increased hydrogen pressure. Further decreasing the hydrogen pressure and raising temperature can facilitate the dehydrogenation of hydrides. The
contents of MgYNi$_4$ increase with the increasing Y content in the ribbons with $x = 1, 3$ and 6.$^{25}$ Mg is consumed by forming MgYNi$_4$ but the hydride of MgYNi$_4$ is not observed in the hydrogenated ribbons. In addition, partial hydrides (such as YH$_2$) do not release hydrogen at the experimental temperature. The maximum dehydrogenation capacity of ribbons with $x = 6$ is lower than that of $x = 3$. The low activation energy of the dehydrogenation reaction makes it easy to release hydrogen. The ribbon with $x = 1$ has the maximum of dehydrogenation capacity in the Mg$_{67}$Ni$_{33}$-$x$Y$_x$ ribbons for the lowest activation energy of the dehydrogenation reaction. But the ribbon with $x = 1$ has relatively high dehydrogenation percent even at 523K. The low activation energy of the dehydrogenation reaction of the Mg$_{67}$Ni$_{33}$-$x$Y$_x$ ($x = 1$) ribbon not only increases the hydrogen desorption capacity and kinetics but decreases the dehydrogenation temperature.

![Fig. 6](image)

**Fig. 6.** Hydrogen desorption content of the Mg$_{67}$Ni$_{33}$-$x$Y$_x$ ribbons.

**Fig. 7** shows the dehydrogenation kinetics curves of the Mg$_{67}$Ni$_{33}$-$x$Y$_x$ ($x = 0, 1, 3, 6$) ribbons at 523 and 623 K in initial 1 and 0.5 h. As can be seen from the kinetics curves, the dehydrogenation rates of ribbons at 523 K are lower than those at 623 K. The increase of temperature improves the dehydrogenation kinetics of ribbons. After the addition of Y, the dehydrogenation kinetics of the Mg$_{67}$Ni$_{33}$-$x$Y$_x$ ($x = 1, 3, 6$) ribbons are better than that of ribbons with $x = 0$ at 523 K. Considering the values of the activation energy of dehydrogenation, the values of Mg$_{67}$Ni$_{33}$-$x$Y$_x$ ($x = 1, 3, 6$) ribbons is lower than that of the ribbon with $x = 0$. The property of dehydrogenation kinetics is related to the activation energy
of dehydrogenation. In addition, the dehydrogenation kinetics is also related to the microstructure of the ribbons. The grain size of ribbons increases with the addition of Y elements. The dehydrogenation kinetics are the results of the activation energy of the dehydrogenation reaction combined with microstructure. The ribbon with \( x = 1 \) has the highest kinetics in the Mg\(_{67}\)Ni\(_{33}\)_\(_x\)Y\(_x\) (\( x = 1, 3, 6 \)) ribbons at 523 and 623 K. The high dehydrogenation kinetics of Mg\(_{67}\)Ni\(_{33}\)_\(_x\)Y\(_x\) ribbons with \( x = 1 \) are also related to the high pore percentage.\(^{25}\)

![Desorption curves of Mg\(_{67}\)Ni\(_{33}\)_\(_x\)Y\(_x\) ribbons](image)

**Fig. 7.** The dehydrogenation kinetics curves of the Mg\(_{67}\)Ni\(_{33}\)_\(_x\)Y\(_x\) (\( x = 0, 1 \)) ribbons at 523 and 623 K in initial 1 and 0.5 h. a) 523 K in initial 1h, b) 623 K in initial 0.5 h.

### 4. Conclusions

The dehydrogenation phase transformation contain Mg\(_2\)NiH\(_4\) to Mg\(_2\)Ni, Mg\(_2\)NiH\(_{0.3}\) to Mg\(_2\)Ni, MgH\(_2\) to Mg and YH\(_3\) to YH\(_2\) of hydrogenated Mg\(_{67}\)Ni\(_{33}\)_\(_x\)Y\(_x\) (\( x = 0, 1, 3, 6 \)) ribbons. Amorphous and nanocrystalline structures and stacking faults are contained in the Mg\(_{67}\)Ni\(_{33}\)_\(_x\)Y\(_x\) (\( x = 0, 1, 3, 6 \)) ribbons. The H element is evenly distributed in the hydrogenated ribbons by EELS analysis. The pores in the melt-spun ribbons are the preferential areas for hydrogenation/dehydrogenation. The pores in metal ribbons generated by melt-spinning facilitate the diffusion of hydrogen, increase dehydrogenation nucleation locations and decrease the diffusion distances. The high dehydrogenation kinetics are the results of low activation energy combined with amorphous and nanocrystalline. The low activation energy...
of the dehydrogenation reaction, caused by melt-spun and addition of Y elements, decreases
the dehydrogenation temperatures and increases the dehydrogenation kinetics of Mg-based
melt-spun ribbons.

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References

1. P. Vajeeston, P. Ravindran, B. C. Hauback, H. Fjellvåg, A. Kjekshus, S. Furuseth and M.
2012, **37**, 3755-3760.
4984-4992.
Hydrogen Energy*, 2013, **38**, 2337-2346.
2010, **35**, 4131-4137.
2013, **38**, 12904-12911.


Captions of figures and tables

Fig. 1. The XRD patterns of the (a) hydrogenated and (b) dehydrogenated Mg_{67}Ni_{33-x}Y_x (x = 0, 1, 3, 6) melt-spun ribbons.

Fig. 2. HRTEM image and SAED pattern of the Mg_{67}Ni_{33-x}Y_x (x = 1, 3, 6) ribbons and EELS hydrogen mapping. a) x = 1, b) x = 3, c) x = 6, d) EELS hydrogen mapping.

Fig. 3. The SEM/BSE images of (a) hydrogenated and (b) dehydrogenated melt-spun ribbons.

Fig. 4. Dehydrogenation DSC and corresponding first derivative curves of the hydrogenated Mg_{67}Ni_{33-x}Y_x (x = 0, 1, 3, 6) melt-spun ribbons. a) heating rate of 10 K/min in Mg_{67}Ni_{33-x}Y_x (x = 0, 1, 3, 6) melt-spun ribbons, b) heating rates of 5, 10, 15 and 20 K/min in x = 1 ribbons.

Fig. 5. Fitted Kissinger curves and corresponding activation energy curves of the hydrogenated Mg_{67}Ni_{33-x}Y_x (x = 0, 1, 3, 6) ribbons in the dehydrogenation. a) fitted Kissinger curves, b) dehydrogenation activation energy curves.

Fig. 6. Hydrogen desorption content of the Mg_{67}Ni_{33-x}Y_x ribbons.

Fig. 7. The dehydrogenation kinetics curves of the Mg_{67}Ni_{33-x}Y_x (x = 0, 1) ribbons at 523 and 623 K in initial 1 and 0.5 h. a) 523 K in initial 1h, b) 623 K in initial 0.5 h.

Table 1. The dehydrogenation peak temperatures of the hydrogenated Mg_{67}Ni_{33-x}Y_x (x = 0, 1, 3, 6) melt-spun ribbons at heating rates of 5, 10, 15 and 20 K/min.