Catalytic effect of MoS$_2$ on hydrogen storage thermodynamics and kinetics of an as-milled YMg$_{11}$Ni alloy

Yanghuan Zhang, $^{*ab}$ Meng Ji,$^{ab}$ Zeming Yuan,$^{ab}$ Wengang Bu,$^{b}$ Yan Qi$^{b}$ and Shihai Guo$^{b}$

In this study, YMg$_{11}$Ni and YMg$_{11}$Ni + 5 wt% MoS$_2$ (named YMg$_{11}$Ni–5MoS$_2$) alloys were prepared by mechanical milling to examine the effect of adding MoS$_2$ on the hydrogen storage performance of a Y–Mg–Ni-based alloy. The as-cast and milled alloys were tested to identify their structures by X-ray diffraction and transmission electron microscopy. The isothermal hydrogen storage thermodynamics and dynamics were identified through an automatic Sieverts apparatus, and the non-isothermal dehydrogenation performance was investigated by thermogravimetry and differential scanning calorimetry. The dehydrogenation activation energy was calculated by both Arrhenius and Kissinger methods. Results revealed that adding MoS$_2$ produces a very slight effect on hydrogen storage thermodynamics but causes an obvious reduction in the hydrogen sorption and desorption capacities because of the deadweight of MoS$_2$. The addition of MoS$_2$ significantly enhances the dehydrogenation performance of the alloy, such as lowering dehydrogenation temperature and enhancing dehydrogenation rate. Specifically, the initial desorption temperature of the alloy hydride lowers from 549.8 K to 525.8 K. The time required to desorb hydrogen at 3 wt% H$_2$ is 1106, 456, 363, and 180 s corresponding to hydrogen desorption temperatures at 593, 613, 633, and 653 K for the YMg$_{11}$Ni alloy, and 507, 208, 125, and 86 s at identical conditions for the YMg$_{11}$Ni–5MoS$_2$ alloy. The dehydrogenation activation energy ($E_a$) values with and without added MoS$_2$ are 85.32 and 98.01 kJ mol$^{-1}$. Thus, a decrease in $E_a$ value by 12.69 kJ mol$^{-1}$ occurs and is responsible for the amelioration of the hydrogen desorption dynamics by adding a MoS$_2$ catalyst.

Introduction

The wide application of hydrogen as a clean fuel is believed to largely offset environmental problems that result from the mass consumption of fossil fuels. The rapid development and extensive application of hydrogen fuel cell vehicles are expected to fundamentally alleviate accelerating global warming and the increasingly serious air pollution because the combustion of fossil fuels is related to the consumption of approximately a quarter of the energy of the whole world$^4$ and the emission of approximately 23% of global CO$_2$.$^2$ However, the application of hydrogen as vehicle fuel is seriously limited, because hydrogen storage systems are not safe and are inefficient.$^3$ In other words, whether the hydrogen fuel cell vehicle will be widely applied in this century depends on its safety, economics, and practical hydrogen storage capacity.$^4$ Storing hydrogen in metal hydrides is the preferred candidate among the known hydrogen storage methods and is expected to make mobile application possible.$^5$ Many hydrogen storage materials have been established, and some of them even have been commercialized on a large scale. These materials are rare earth-based AB$_5$ and Laves-phase AB$_2$ alloys. However, selecting which material could satisfy the performance requirements for vehicular application presented by the U.S. Department of Energy is difficult.$^6$ Concerning hydrogen storage capacity, Mg and Mg-based alloys show their preponderances for on-board hydrogen fuel cell.$^7$ However, the practical application of Mg and Mg-based alloys is restricted severely by some inherent disadvantages, including the high thermodynamic stability and slow hydrogen absorption/desorption dynamics. Therefore, the researchers must exert considerable effort to further improve these hydrogen storage properties of the Mg-based alloys.

Based on the summary of numerous literatures, the two major approaches to improve the Mg and Mg-based alloys in hydrogen storage performances are reducing the particle size and adding catalysts (elements or compounds) to form Mg-based composites or solid solution. Ouyang et al.$^8$–$^{10}$ found the P-milling technique can tune thermodynamic and kinetic
properties of Mg-based hydrogen storage materials. The structures of Mg and Mg-based alloys have obvious effects on their hydrogen absorption/desorption thermodynamics and dynamics.\(^1\) The formation of composite microstructures can substantially improve the hydrogen storage properties of Mg-based alloys.\(^2\) In particular, when the grain sizes of Mg-based alloys are far below micrometer scale, their hydriding/dehydriding performances will be improved dramatically.\(^3\)\(^,\)\(^4\) Kumar et al.\(^5\) found that ultrafine microstructure (sub 100 nm range) decreases Mg\(_2\)Ni alloy by 100 K in the hydrogen absorption/desorption temperature, that is, from 573 K to 473 K. This result was also affirmed by Cheung et al.\(^6\) that the stability of MgH\(_2\) drops quickly when its particle size reduces to nanoscale. The hydrogen atom diffusion distance for traversing the hydride is shortened relatively as a result of the small scales and high surface area-to-volume ratio belonging to the nanostructured powders, thereby improving the hydrogenation dynamics by several times and even more.\(^7\) Some synthetic methods, such as arc plasma,\(^8\) equal channel angular pressing (ECAP),\(^9\) inert gas condensation (IGC),\(^10\) hydriding combustion synthesis,\(^11\) mechanical milling,\(^12\)\(^,\)\(^13\) and rapid solidification (RS),\(^14\)\(^,\)\(^15\) have been widely used in the syntheses of different amorphous and nanocrystalline Mg-based alloys with various ingredients. Among all of the techniques, mechanical milling and melt spinning are considered to be fairly effective by which the amorphous and/or nanocrystalline alloys can be obtained with homogeneous element distributions. Poletaev et al.\(^16\) prepared the LaMg\(_{11}\)Ni alloy using rapid solidification technology and found that LaMg\(_{11}\)Ni alloy that solidified at the highest cooling rate exhibited the best hydriding dynamics and reached the maximal hydrogen absorption capacity of 5.02 wt% H\(_2\). Jeon et al.\(^17\) prepared a composite, of which the Mg nanoparticle was more than 60 wt% and dispersed in a dissolved polymer. They also found that the hydrogen absorption and desorption could occur in this composite with a fast dynamics below 473 K.

In general, rare earth elements,\(^18\) transition metallic elements\(^19\) and their oxides,\(^20\)\(^,\)\(^21\) fluorides,\(^22\)\(^,\)\(^23\) halides,\(^24\) hydrides,\(^25\) and intermetallic compounds,\(^26\) are good catalysts that can destabilize MgH\(_2\) and enhance the hydriding and dehydriding rate of the alloy hydrides. The dissociation of hydrogen molecules on the Mg surface is considered a rate-controlling factor for dehydrogenation because of the high energy (1.15 eV) required. This dissociation energy can be reduced by adding catalysts. For example, the presence of transition metals, such as Pd, Cu, Ni, and Co, can reduce dissociation energy to 0.39, 0.56, 0.06, and 0.03 eV, respectively.\(^27\) Theoretically, the substitutional atoms in MgH\(_2\) can cause an interaction between the valence electron of H and the unsaturated d/f electron shells of transition metals, which will weaken the Mg–H bond. Thus, the hydrogen desorption behavior of MgH\(_2\) is ameliorated significantly.\(^28\) In addition, some catalysts with high hardness also play the role of cracking agent during ball milling so that the size of alloy particles can be reduced dramatically.\(^29\) The advantage of effect of reducing particle size on hydrogen sorption and desorption properties has been described. Sadhasivam et al.\(^30\) investigated the effect of adding Mn (the major ingredients are Ce and La) oxide on the dehydrogenation dynamics of MgH\(_2\) and found that it improved hydrogenation behavior. The initial dehydrogenation temperature for MgH\(_2\) catalyzed by 5 wt% Mn oxide obtained a decrease of 349 K, that is, from 654 K (ball-milled) to 578 K. Daryani et al.\(^31\) reported that adding TiO\(_2\) catalysts can significantly enhance the milling efficiency and accelerate the size reduction of MgH\(_2\) during ball milling. Moreover, the addition of 6 mol% TiO\(_2\) markedly improved the hydrogen absorption dynamics and decreased the decomposition temperature of as-milled MgH\(_2\) by 373 K.

Our previous work has investigated the thermodynamics and dynamics of the REMg\(_{11}\)Ni (RE = La, Nd, Pr) + x wt% Ni (x = 100, 200) alloys and found that Ni addition exhibits an effective catalytic action on ameliorating the hydrogen storage properties of REMg\(_{11}\)Ni (RE = La, Nd, Pr) alloys.\(^32\)\(^,\)\(^33\) However, the hydrogenation thermodynamics and dynamics ameliorated by adding Ni negatively affected capacity. Han et al.\(^34\)\(^,\)\(^35\) found MoS\(_2\) has superior properties on catalyzing the hydriding/dehydriding kinetics of MgH\(_2\) and markedly decreases the decomposition temperature of LiBH\(_4\). To avoid the lowering of hydrogen adsorption capacity because of excessive Ni, a trace of MoS\(_2\) is added in YMg\(_{11}\)Ni as catalyst. In the present work, YMg\(_{11}\)Ni alloy is investigated for its phase composition, microstructure, catalytic hydrogen desorption temperature, and activation energy to study the effects of MoS\(_2\) on hydrogen storage thermodynamics and kinetics of as-milled YMg\(_{11}\)Ni alloy.

**Experimental**

YMg\(_{11}\)Ni alloy was prepared in a vacuum induction furnace with 0.04 MPa protective gas of helium for preventing the volatilization of Mg. The liquid alloy was cast into ingots with a cooled copper mould. Portions of the ingots were severed and crushed into powders with diameters of approximately 50 μm. After crushing, 5 wt% MoS\(_2\) (particle size ≤ 30 nm, Sinopharm Chemical Reagent Co., Ltd) was added and a planetary-type mill was used for milling this mixed powder. During ball milling, the argon atmosphere was selected to fill up the mill to prevent the oxidation of mixed powders. In this experiment, the ball-to-powder weight ratio was 35 : 1, in which the balls and powders were placed into Cr–Ni stainless steel vials and ran at 135 rpm for 20 h. During the whole process, the mill had a 10 min rest after every 60 min milling to prevent overheating.

The X-ray diffraction (XRD) (D/max2400) equipped with CuK\(_{a1}\) radiation filtered by graphite was used to test the as-cast and milled alloys of their phase structures. The experimental parameters of XRD were set at 160 mA, 40 kV, and 10\(^{\circ}\) min\(^{-1}\). High-resolution transmission electron microscope (HRTEM) (JEM-2100F) was used to observe the powder samples at 200 kV. Electron diffraction (ED) was used to ascertain their crystalline states.

An automatically controlled Sieverts apparatus was used to measure the isothermal hydriding and dehydriding dynamics with the temperature error controlled within ±2 K. The weight of samples for each measurement was 300 mg. The hydrogenation reaction proceeded in 3 MPa hydrogen (initial pressure
for hydrogenation reaction) at 593, 613, 633, and 653 K, at similar temperatures at which the dehydrogenation process proceeded with the hydrogen pressure setting at $1 \times 10^{-4}$ MPa. Thermogravimetry and differential scanning calorimetry (DSC) (SDT-Q600) were used to investigate the non-isothermal dehydrogenation performance with heating rates setting at 5, 10, 15, and 20 K min$^{-1}$. The temperature programmed desorption (TDP) performance of the hydrogenation saturated alloys was test by thermogravimetry measurement under dynamic heating condition (5 K min$^{-1}$) and 35.1 mL min$^{-1}$ high-purity argon (99.999%) flow rate.

Results and discussion
Structure characteristics

Fig. 1 shows the XRD curves of the as-cast and milled YMg$_{11}$Ni and YMg$_{11}$Ni + 5 wt% MoS$_2$ alloys before and after hydrogenation and dehydrogenation. The hydrogenation reaction occurred at 593 K and 3 MPa, whereas dehydrogenation reaction occurred at 593 K and $1 \times 10^{-4}$ MPa. The XRD pattern of alloys were identified by ICDD, and the results revealed that two phases appear inside the as-cast alloy, including Mg$_{24}$Y$_5$ and Mg$_2$Ni as the major and secondary phases, respectively. Mechanical milling causes diffraction peaks to merge and dramatically broaden, as well as show a typical nanocrystalline and amorphous structure. After adding MoS$_2$, the diffraction peaks become more broaden, which means the more serious refinement of grains, as Fig. 1(b) shows. After hydrogenation, the alloy exhibits an obvious crystalline reaction, and three hydrides can be found in the YMg$_{11}$Ni alloy. The hydrides are MgH$_2$, Mg$_2$NiH$_4$, and YH$_3$. Based on XRD analysis, possible formation pathways of the hydrides can be inferred as follows:

$$\begin{align*}
\text{Mg}{}_{24}\text{Y}_5 + \text{H}_2 & \rightarrow \text{MgH}_2 + \text{YH}_2 \\
\text{YH}_2 + \text{H}_2 & \rightarrow \text{YH}_3 \\
\text{Mg}_2\text{Ni} + \text{H}_2 & \rightarrow \text{Mg}_2\text{NiH}_4
\end{align*}$$

Three phases appear in the dehydrogenated YMg$_{11}$Ni alloy, including YH$_2$, Mg, and Mg$_2$Ni. The path of the dehydrogenation reaction can be inferred as follows:

$$\begin{align*}
\text{MgH}_2 & \rightarrow \text{Mg} + \text{H}_2 \\
\text{Mg}_2\text{NiH}_4 & \rightarrow \text{Mg}_2\text{Ni} + \text{H}_2 \\
\text{YH}_3 & \rightarrow \text{YH}_2 + \text{H}_2
\end{align*}$$

YH$_2$ phase remains undecomposed, which is due to its high thermal stability. Fig. 1(b) shows that adding MoS$_2$ catalyst does not create any new phase in the pattern, suggesting no reaction between the MoS$_2$ and any element in the alloy. From the abovementioned results, the reversible reactions during the hydrogenation and dehydrogenation processes include the following reactions:

$$\begin{align*}
\text{Mg} + \text{H}_2 & \leftrightarrow \text{MgH}_2 \\
\text{Mg}_2\text{Ni} + \text{H}_2 & \leftrightarrow \text{Mg}_2\text{NiH}_4 \\
\text{YH}_2 + \text{H}_2 & \leftrightarrow \text{YH}_3
\end{align*}$$

The HRTEM images and ED patterns of the as-milled YMg$_{11}$Ni and YMg$_{11}$Ni–5MoS$_2$ alloys before and after
hydrogenation and dehydrogenation are shown in Fig. 2. The as-milled YMg11Ni alloy has a nanocrystalline and amorphous structure with particle size of approximately 15 nm in average. The mechanical milling does not change the alloy of its phase composition, containing the Mg24Y and Mg2Ni phases, which are also affirmed by the ED patterns analysis. After hydrogenation, the as-milled YMg11Ni alloy still shows a nanocrystalline and amorphous structure (Fig. 2(b)), but the amorphous phase obviously decreases, suggesting that hydrogen absorption facilitates the crystalline reaction. Three hydrides, namely, MgH2, Mg2NiH4, and YH3, appear in the hydrogenated alloy, which is supported by ED patterns. Fig. 2(c) shows that the dehydrogenated YMg11Ni alloy shows a completely crystalline structure, and the grain sizes visibly grow. Pukazhvelan et al.22 have noticed a similar phenomenon. The structural analysis and ED rings index revealed that three phases appear in the dehydrogenated YMg11Ni alloy, namely, Mg, Mg2Ni, and YH2. Apparently, YH2 maintains undecomposed in the process of hydrogen desorbed, which is consistent with XRD detection. Fig. 2(d) shows that the as-milled YMg11Ni–5MoS2 alloy has a nanocrystalline structure, but compared with the undoped MoS2 alloy, the grain size is obviously diminished (Fig. 2(a)), suggesting that adding MoS2 catalyst can enhance the ball milling efficiency. The soft MoS2 particles are excellent lubrication, which can inhibit the agglomeration and cold welding of alloy particles during milling.

**P–C–T curves and hydrogen storage thermodynamics**

Fig. 3 shows the P–C–T curves of the as-milled YMg11Ni and YMg11Ni–5MoS2 alloys at 593, 613, 633, and 653 K by which the effect of adding MoS2 on the hydrogenation/dehydrogenation thermodynamics can be examined. The absorbing and desorbing pressure plateaus of the alloys are fairly flat, and the hysteresis (\(H_T = \ln(P_a/P_d)\)) is relatively small. The addition of MoS2 catalyst has an insignificantly effect on the plateau features of the P–C–T curves. Two pressure plateaus appear in each P–C–T curve. The higher pressure plateau corresponds to the Mg2NiH4, the lower one is MgH2 that is according to the reported results,47 which is demonstrated in Mg–10Ni–xMn

![Fig. 2](image-url)

**Fig. 2** HRTEM micrographs and SAD patterns of the as-milled alloys at different states: (a) as-milled YMg11Ni, (b) hydrogenated YMg11Ni, (c) dehydrogenated YMg11Ni, (d) as-milled YMg11Ni–5MoS2, (e) hydrogenated YMg11Ni–5MoS2, (f) dehydrogenated YMg11Ni–5MoS2.
Van’t Hoff graphs of ln[$P(H_2)/P_0$] versus $1/T$ for the YMg$_{11}$Ni and YMg$_{11}$Ni–5MoS$_2$ alloys can be plotted using the logarithmic transform of eqn (1), as inserted in Fig. 3. With the aid of Van’t Hoff plots, the thermodynamic parameters can be calculated conveniently, as listed in Table 1.

These findings indicate that ball milling can reduce the absolute value of hydrogen desorption thermodynamic parameters, and the addition of MoS$_2$ catalyst into YMg$_{11}$Ni alloy incurs a further reduction. In addition, the obtained dehydrogenation enthalpies ($\Delta H_{de}$) and entropies ($\Delta S_{de}$) of the second phase are consistent with the reported values of Mg$_2$NiH$_4$ in the range of 53.23–72.9 kJ mol$^{-1}$.$^{26}$ The dehydrogenation enthalpies ($\Delta H_{de}$) and entropies ($\Delta S_{de}$) of Mg$_2$NiH$_4$ in YMg$_{11}$Ni–5MoS$_2$ are 54.74 kJ mol$^{-1}$ and 113.43 J (K$^{-1}$ mol$^{-1}$), respectively, which are much lower than those of Mg$_2$NiH$_4$ in as-milled YMg$_{11}$Ni alloy (64.5 kJ mol$^{-1}$, 122.3 J (K$^{-1}$ mol$^{-1}$)).$^{26}$ Let alone in as-cast YMg$_{11}$Ni alloy (63.32 kJ mol$^{-1}$, 94.89 J (K$^{-1}$ mol$^{-1}$)). As considered by Agarwal et al.,$^{26}$ the obvious thermodynamic improvement, that is, the destabilization of MgH$_2$, can be achieved only by reducing the grain size to less than 5 nm, which is difficult to realize by mechanical milling. Cheung et al.$^{46}$ concluded through theoretical calculation that when the grain size of MgH$_2$ reduces to approximately 1 nm, its stability will drop drastically. Further study revealed that the thermodynamic change could hardly occur unless its grain size is less than 2 nm. However, Paskevicius et al.$^{51}$ concluded that MgH$_2$ has lesser stability when the particle size is approximately 7 nm than the bulk material, whereas Anik et al.$^5$ considered that the addition of transition metals into Mg or alloying with Mg will considerably ameliorate magnesium hydride in its thermodynamics.

### Hydrogenation and dehydrogenation dynamics

For investigating the effect of adding MoS$_2$ on hydrogenation dynamics, the variations of hydrogenation capacity of the as-milled YMg$_{11}$Ni and YMg$_{11}$Ni–5MoS$_2$ alloys with hydriding reaction time were measured at 3 MPa and different temperatures at 593, 613, 633, and 653 K, as presented in Fig. 4. In the initial stage, the as-milled alloys showed a high hydrogen-absorbing rate. Subsequently, the hydrogen content took a long time to reach saturation. The circumstance that determines the hydrogenation curve characteristics is probably that at which the alloy obtains a hydride layer on its surface in the initial few minutes that may prevent hydrogen from further diffusion and limit the reaction rate. The addition of MoS$_2$ catalyst engenders a positive contribution to the enhancement
of the hydrogen absorption rate of YMg11Ni alloy. From Fig. 4, the hydrogenation capacities within 60 s at 593, 613, 633, and 653 K are 4.076, 4.399, 4.559, and 4.714 wt%, respectively, for the YMg11Ni alloy and 4.364, 4.422, 4.616, and 4.828 wt%, respectively, for the YMg11Ni–5MoS2 alloy. The addition of MoS2 compound incurs an obvious catalytic effect on the hydrogenation properties of the alloy. The hydrogenation process of MgH2 is governed by three critical steps, namely, (a) the dissociation of H2 from molecule to atom on Mg surface, (b) the diffusion of H atoms along the crystal boundary, and (c) the hydrogenation/dehydrogenation of catalyst and Mg atoms and the transformation of MgH2 at catalyst/Mg interface. Among all of these steps, step (a) is considered as the rate-controlling factor because of the high energy it requires. Chen et al. have reported that atomic Fe can catalyze the dehydrogenation of MgH2 most because of its polyvalency and moderate strength of electron attraction. Similar to Fe, Mo also has polyvalency. Moreover, Jia et al. have demonstrated that Mo is able to facilitate the dissociation of hydrogen. Barkhordarian et al. proved that the addition of some catalysts, such as transition metal oxides or sulfide, incurs a decline in this dissociation energy. Therefore, adding MoS2 particles is speculated to accelerate step (a), that is, facilitate hydrogen dissociation from molecules into atoms. MoS2 covered on fine alloy grains provides many channels to penetrate hydrogen and active nucleation sites to form MgH2. Moreover, the added MoS2 can work as lubricant, which inhibits the agglomeration and cold welding, and improve the effects of ball milling, including the decrease in particle size and increase in surface area-to-volume ratio, consequently facilitating H atoms passing through the hydride and significantly improving the hydrogenation and dehydrogenation dynamics.

At a heating rate of 5 K min⁻¹ in a closed chamber, the temperature programmed desorption curve of the as-milled YMg11Ni and YMg11Ni–5MoS2 alloys, which are hydrogenation saturated at 593 K and 3 MPa, were tested as shown in Fig. 5. As the increased pressure can affect the desorption temperature, equal weights of samples were prepared for comparison to avoid this error. Fig. 5 shows that the initial desorption temperature of the as-milled YMg11Ni alloy is approximately 549.8 K, and the total dehydrogenation capacity is 5.286 wt% H2 by 696 K. The addition of MoS2 can reduce the initial desorption temperature to approximately 525.8 K. It supports the view of Rafi-ud-din et al. that adding catalyst can affect the MgH2 in initial desorption temperature. The improved desorption behavior, such as the decreased initial dehydrogenation temperature of the alloy, caused by adding MoS2 might be ascribed to the weakened Mg–H bond that is caused by the electronic exchange reaction between the catalyst and MgH2, and the similar results have been demonstrated in MgH2 coated by multi-valence Ti.

To examine the effect of adding MoS2 on the as-milled YMg11Ni alloy in hydrogen desorption dynamics, isothermal dehydrogenation measurements of the YMg11Ni and YMg11Ni–5MoS2 alloys were conducted at different temperatures, as depicted in Fig. 6. The different temperatures for the isothermal dehydrogenation curves are 593, 613, 633, and 653 K. The temperature variation incurs a significant influence on dehydrogenation dynamics. The increase in temperature dramatically enhances the hydrogen desorption rate of alloys. Fig. 6 shows that the time required by desorbing 3 wt% H2 at 593, 613,
Adding MoS$_2$ generates a positive contribution to the hydrogen desorption rate of YMg$_{11}$Ni alloy. To explore the mechanism of this contribution, Arrhenius and Kissinger methods were incurred for estimating the dehydrogenation activation energy of YMg$_{11}$Ni and YMg$_{11}$Ni–5MoS$_2$ alloys. The dehydrogenation dynamics is assumed to be connected with the energy barrier for MgH$_2$ releasing H$_2$. In general, the total energy barrier that the reaction requires to conquer is signified by activation energy. As for dehydrogenation reaction, the activation energy of which is considered to be related to the whole energy barriers concerning dehydrogenation processes. Therefore, the driving force of a dehydrogenation reaction can be determined by calculating activation energy. The hydrogen desorption reaction is performed through a nucleation and growth processes, which can be simulated by Johnson–Mehle–Avramie (JMA) model and described by the following formula:\(^5\)

$$\ln[-\ln(1 - \alpha)] = \eta \ln k + \eta \ln t$$ \hspace{1cm} (2)

where $\alpha$ stands for the phase fraction transformed at time $t$, $\eta$ stands for the Avrami exponent, and $k$ stands for an effective dynamic parameter. The JMA graphs of $\ln[-\ln(1 - \alpha)]$ versus $\ln t$ at 593, 613, 633, and 653 K can be constructed using the logarithmic transformation of eqn (2), as illustrated in Fig. 7. The JMA plots are nearly linear, implying that the dehydridding reaction of alloys includes instantaneous nucleation and interface-controlled three-dimensional growth process.\(^6\) Thus, the $\eta$ and $\ln k$ values at different temperatures can be derived from the slope and intercept of the JMA plots, from which the rate constant ($k$) could be calculated expediently. According to the Arrhenius equation, the activation energy $E_a(de)$ for the dehydrogenation process can be computed as follows:\(^6\)

$$k = A \exp[-E_a(de)/RT]$$ \hspace{1cm} (3)

where $k$ stands for rate constant that has been defined previously, $A$ stands for a temperature-independent coefficient, $R$ stands for the universal gas constant, and $T$ stands for the absolute temperature. The Arrhenius plots of $\ln k$ versus $1/T$ for the dehydrogenation dynamics of the alloys are described in Fig. 7. Therefore, the activation energy $E_a(de)$ can be derived from the slopes of the Arrhenius plots. The $E_a(de)$ values of the as-milled YMg$_{11}$Ni and YMg$_{11}$Ni–5MoS$_2$ alloys are 98.01 and 85.32 kJ mol$^{-1}$, respectively. The reduction of 12.7 kJ mol$^{-1}$ occurs in the activation energy, and the similar result has been obtained in CeH$_{2.73}$–MgH$_2$–Ni composites, which displays about 41.4 kJ mol$^{-1}$ reduction.\(^4\) This is thought to be the result of the high-density interfacial energy between Mg phase and MoS$_2$ phase in the YMg$_{11}$Ni alloy embedded by MoS$_2$ nanoparticles, 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 system alloys, the decrease of activation energy caused by high-density interface required for effective catalysis has been found as well.\(^5\,7\,8\,9\,60\)

Simultaneously, the hydrogen desorption activation energy is also calculated in Kissinger method for comparison with the following equation: \(^6\)

$$d[\ln(\beta/T_p^\beta/T_P^\beta)]/d(1/T_P) = -E_a(de)/R$$ \hspace{1cm} (4)

where $\beta$ stands for the heating rate, $T_p$ stands for the absolute temperature at which the DSC curve reaches the top desorption rate, $E_a(de)$ stands for activation energy, and $R$ stands for the ideal gas constant. The DSC measurement is indispensable in the Kissinger method, thus the non-isothermal dehydrogenation reactions of as-milled YMg$_{11}$Ni and YMg$_{11}$Ni–5MoS$_2$ alloys that hydrogenated at 593 K and 3 MPa were measured by DSC.
with heating rates at 5, 10, 15, and 20 K min\(^{-1}\), respectively. Results are presented in Fig. 8. During the hydrogenation process, there exists a clear endothermic peak, which is attributed to the dehydrogenation of MgH\(_2\) phase. The endothermic peaks of Mg\(_2\)NiH\(_4\)/Mg\(_2\)Ni and YH\(_3\)/YH\(_2\) phase transition cannot be verified, which is most likely due to low content of Mg\(_2\)NiH\(_4\) and YH\(_3\) in the sample, as well as their endothermic peaks cover the same temperature range. Moreover, the shapes of all endothermic peaks are similar, which indicates that the reaction processes of hydrogenation for all alloys are similar. In addition, the endothermic peak of MoS\(_2\)-added alloy drifts to low temperature compared with the no-MoS\(_2\)-added alloy at each heating rate, which reflects the improvement of adding MoS\(_2\) in the reaction rate of dehydrogenation. Based on the data of Fig. 8, the graphs of \(\ln(\beta/T_F)/T_F\) versus \(1/T_F\) can be constructed using the logarithmic transformation of eqn (4), which is termed as Kissinger plots as inserted in Fig. 8. The Kissinger plots are nearly linear, from the slopes of which the activation energy \(E_a\) of dehydrogenation is an important indicator in which the dehydrogenation performances and catalytic effects of catalysts can be evaluated. From the reduction of activation energy \(E_a\), we can deduce the reduction of energy barriers for systems releasing hydrogen.

**Conclusions**

(1) The addition of MoS\(_2\) can reduce the as-milled YMg\(_{11}\)Ni alloy in thermodynamic parameters (\(\Delta H\) and \(\Delta S\)). Furthermore, it weakens the stability of the alloy hydride. As can be observed from the experiment, the initial dehydrogenation temperature of the YMg\(_{11}\)Ni hydrogenated is declined from 549.8 K to 525.8 K by adding MoS\(_2\).
(2) The addition of MoS$_2$ significantly enhances the alloy in the hydrogen absorbing and desorbing rates, which are connected with the diminished particle sizes and the declined dehydrogenation activation energy generated by adding MoS$_2$.

(3) The dehydrogenation activation energies of the as-milled YMg$_{11}$Ni and YMg$_{11}$Ni$_2$MоS$_2$ alloys have been evaluated in both Arrhenius and Kissinger methods. Results revealed that the addition of MoS$_2$ can decrease the alloys in dehydrogenation activation energy, which is considered as the real driver for improving the dehydrogenation dynamics of the alloys by adding MoS$_2$.

Acknowledgements

This work is financially supported by the National Natural Science Foundations of China (51371094 and 51471054) and Natural Science Foundation of Inner Mongolia, China (2015MS0558).

References

1 D. Mori and K. Hirose, *Int. J. Hydrogen Energy*, 2009, 34, 4569–4574.
2 R. Lan, J. T. S. Irvine and S. Tao, *Int. J. Hydrogen Energy*, 2012, 37, 1482–1494.
3 L. Zhou, *Renewable Sustainable Energy Rev.*, 2005, 9, 395–408.
4 V. Bhat, A. Roguier, L. Aymard, G. A. Nazri and J. M. Tarascon, *Int. J. Hydrogen Energy*, 2007, 32, 4900–4906.
5 M. Anik, F. Karanfil and N. Küçükdeveci, *Int. J. Hydrogen Energy*, 2012, 37, 299–308.
6 T. Umegaki, J. M. Yan, X. B. Zhang, H. Shioyama, N. Kuriyama and Q. Xu, *Int. J. Hydrogen Energy*, 2009, 34, 2303–2311.
7 L. Z. Ouyang, J. J. Tang, Y. J. Zhao, H. Wang, X. D. Yao, J. W. Liu, J. Zou and M. Zhu, *Sci. Rep.*, 2015, 5, 10776.
8 L. Z. Ouyang, Z. J. Cao, H. Wang, R. Z. Hu and M. Zhu, *J. Alloys Compd.*, 2017, 691, 422–435.
9 L. Z. Ouyang, Z. J. Cao, H. Wang, J. W. Liu, D. L. Sun, Q. A. Zhang and M. Zhu, *J. Alloys Compd.*, 2014, 586, 113–117.
10 L. Z. Ouyang, Z. J. Cao, H. Wang, J. W. Liu, D. L. Sun, Q. A. Zhang and M. Zhu, *Int. J. Hydrogen Energy*, 2013, 38, 8881–8887.
11 A. Teresiak, A. Gebert, M. Savyak, M. Uhlemann, C. Mickel and N. Mattern, *J. Alloys Compd.*, 2005, 398, 156–164.
12 M. Zhu, H. Wang, L. Z. Ouyang and M. Q. Zeng, *Int. J. Hydrogen Energy*, 2006, 31, 251–257.
13 T. Sadasivam, M. S. L. HUDSO, S. K. Pandey, A. Bhatnagar, M. K. Singh, K. Gurunathan and O. N. Srivastava, *Int. J. Hydrogen Energy*, 2013, 38, 7353–7362.
14 S. Kalininchenka, L. Röntzsch, T. Riedl, T. Gemming, T. Weißgärber and B. Kieback, *Int. J. Hydrogen Energy*, 2011, 36, 1592–1600.
15 L. H. Kumar, B. Viswanathan and S. S. Murthy, *J. Alloys Compd.*, 2008, 461, 72–76.
16 S. Cheung, W. Q. Deng, A. C. T. Duin and W. A. Goddard, *J. Phys. Chem. A*, 2005, 109, 851–859.
17 J. Huot, G. Liang, S. Boily, A. V. Neste and R. Schulz, *J. Alloys Compd.*, 1999, 293–295, 495–500.
18 J. X. Zou, X. Q. Zeng, Y. J. Ying, X. Chen, H. Guo, S. Zhou and W. J. Ding, *Int. J. Hydrogen Energy*, 2013, 38, 2337–2346.
19 M. Jorge Jr, E. Prokoffiev, G. F. Lima, E. Rauch, M. Veron, W. J. Botta, M. Kawasaki and T. G. Langdon, *Int. J. Hydrogen Energy*, 2013, 38, 8306–8312.
20 M. Calizzi, D. Chericoni, L. H. Jepsen, T. R. Jensen and L. Pasquin, *Int. J. Hydrogen Energy*, 2016, 41, 14447–14454.
21 H. Gu, Y. Zhu and L. Li, *Int. J. Hydrogen Energy*, 2008, 33, 2970–2974.
22 D. Pukazhselvan, G. Capurso, A. Maddalena, S. L. Russo and D. P. Fagg, *Int. J. Hydrogen Energy*, 2014, 39, 20045–20053.
23 Y. H. Zhang, X. Y. Han, B. W. Li, H. P. Ren, X. P. Dong and X. L. Wang, *Mater. Charact.*, 2008, 59, 390–396.
24 S. Kalininchenka, L. Röntzsch, T. Riedl, T. Weißgärber and B. Kieback, *Int. J. Hydrogen Energy*, 2011, 36, 10808–10815.
25 Y. H. Zhang, Rafi-ud-din, B. W. Li, H. P. Ren, S. H. Guo and X. L. Wang, *Mater. Charact.*, 2010, 61, 305–311.
26 A. A. Poletaev, R. V. Denys, J. P. Maehlen, J. K. Solberg, B. P. Tarasov and V. A. Yartys, *Int. J. Hydrogen Energy*, 2012, 37, 3548–3557.
27 K. J. Jeon, H. R. Moon, A. M. Ruminski, B. Jiang, C. Kisielowski and R. Bardhan, *Nat. Mater.*, 2011, 10, 286–290.
28 M. Tanniru and F. Ebrahimi, *Int. J. Hydrogen Energy*, 2009, 34, 7714–7723.
29 S. Long, J. X. Zou, X. Chen, X. Q. Zeng and W. J. Ding, *J. Alloys Compd.*, 2014, 615, S684–S688.
30 Rafi-ud-din, X. H. Qu, P. Li, Z. Lin, A. Mashkoor, I. M. Zubair, M. Yasir Rafique and F. M. Hassan, *RSC Adv.*, 2012, 2, 4891–4903.
31 N. Juahir, N. S. Mustafa, A. M. Sinin and M. Ismail, *RSC Adv.*, 2015, 5, 60983–60989.
32 H. Z. Liu, C. Wu, H. Zhou, T. Chen, Y. G. Liu, X. H. Wang, Z. H. Dong, H. W. Ge, S. Q. Li and M. Yan, *RSC Adv.*, 2015, 5, 22091–22096.
33 X. J. Hou, R. Hu, T. B. Zhang, H. C. Kou, W. J. Song and J. S. Li, *Int. J. Hydrogen Energy*, 2014, 39, 19672–19681.
34 E. Malka, T. Czujko and J. Bystrzycki, *Int. J. Hydrogen Energy*, 2010, 35, 1706–1712.
35 F. P. Luo, H. Wang, L. Z. Ouyang, M. Q. Zeng, J. W. Liu and M. Zhu, *Int. J. Hydrogen Energy*, 2013, 38, 10912–10918.
36 S. Agarwal, A. Jain, P. Jain, M. Jangir, D. Vyas and I. P. Jain, *J. Alloys Compd.*, 2015, 645, S518–S523.
37 M. Pozzo and D. Alfe, *Int. J. Hydrogen Energy*, 2009, 34, 1922–1930.
38 T. Liu, T. W. Zhang, X. Z. Zhang and X. G. Li, *Int. J. Hydrogen Energy*, 2011, 36, 3515–3520.
39 Rafi-ud-din, H. Qu, G. H. Zahid, Z. Asghar, M. Shahzad, M. Iqbal and E. Ahmad, *J. Alloys Compd.*, 2014, 604, 317–324.
40 M. Daryani, A. Simchi, M. Sadati, H. M. Hosseini, H. Targholizadeh and M. Khakbizz, *Int. J. Hydrogen Energy*, 2014, 39, 21007–21014.
41 Y. H. Zhang, Z. M. Yuan, W. G. Bu, F. Hu, Y. Cai and D. L. Zhao, *Acta Metall. Sin.*, 2016, 29, 577–586.
42 Y. H. Zhang, B. W. Li, H. P. Ren, T. Yang, S. H. Guo, Y. Qi and D. L. Zhao, J. Mater. Sci. Technol., 2016, 32, 218–225.
43 Y. H. Zhang, Z. M. Yuan, T. Yang, D. C. Feng, Y. Cai and D. L. Zhao, J. Alloys Compd., 2016, 688, 585–593.
44 Y. H. Jia, S. M. Han, W. Zhang, X. Zhao, P. F. Sun, Y. Q. Liu, H. Shi and J. S. Wang, Int. J. Hydrogen Energy, 2013, 38, 2352–2356.
45 D. Liang, S. M. Han, J. S. Wang, W. Zhang, X. Zhao and Z. Y. Zhao, J. Solid State Chem., 2014, 211, 21–24.
46 T. Yang, Z. M. Yuan, W. G. Bu, Z. C. Jia, Y. Qi and Y. H. Zhang, Int. J. Hydrogen Energy, 2016, 41, 2689–2699.
47 Q. Luo, Q. F. Gu, J. Y. Zhang, S. L. Chen, K. C. Chou and Q. Li, Sci. Rep., 2015, 5, 15385.
48 J. G. Yuan, N. Xing and Y. Wu, Int. J. Hydrogen Energy, 2017, 42, 6118–6126.
49 H. Falahati and P. J. B. Dominik, Int. J. Hydrogen Energy, 2013, 38, 8838–8851.
50 L. Z. Ouyang, Z. J. Cao, H. Wang, J. W. Liu, D. L. Sun, Q. A. Zhang and M. Zhu, Int. J. Hydrogen Energy, 2013, 38, 8881–8887.
51 M. Paskevicius, D. A. Sheppard and C. E. Buckley, J. Am. Chem. Soc., 2010, 13, 25077–25083.
52 P. Jain, Int. J. Hydrogen Energy, 2009, 34, 7368–7378.
53 H. P. Chen, H. Yu, Q. Q. Zhang, B. G. Liu, P. Liu, X. P. Zhou, Z. Y. Han and S. X. Zhou, J. Power Sources, 2016, 322, 179–186.
54 Y. H. Jia, S. M. Han, W. Zhang, X. Zhao, P. F. Sun, Y. Q. Liu, H. Shi and J. S. Wang, Int. J. Hydrogen Energy, 2013, 38, 2352–2356.
55 G. Barkhordarian, T. Klassen and R. Bormann, J. Alloys Compd., 2004, 364, 242–246.
56 E. A. Lass, Int. J. Hydrogen Energy, 2011, 36, 10787–10796.
57 J. Cui, H. Wang, J. W. Liu, L. Z. Ouyang, Q. G. Zhang, D. L. Sun, X. D. Yao and M. Zhu, J. Mater. Chem. A, 2013, 1, 5603–5611.
58 M. Pourabdoli, S. Raygan, H. Abdizadeh and D. Uner, Int. J. Hydrogen Energy, 2013, 38, 11910–11919.
59 T. Czujko, R. A. Varin, C. Chiu and Z. Wronski, J. Alloys Compd., 2006, 414, 240–247.
60 T. Kimura, H. Miyaoka, T. Ichikawa and Y. Kojima, Int. J. Hydrogen Energy, 2013, 38, 13728–13733.
61 L. Z. Ouyang, X. S. Yang, M. Zhu, J. W. Liu, H. W. Dong, D. L. Sun, J. Zou and X. D. Yao, J. Phys. Chem. C, 2014, 118, 7808–7820.
62 L. Z. Ouyang, F. X. Qin and M. Zhu, Scr. Mater., 2006, 55, 1075–1078.
63 L. Z. Ouyang, F. X. Qin and M. Zhu, Scr. Mater., 2009, 61, 339–342.
64 L. Z. Ouyang, S. Y. Ye, H. W. Dong and M. Zhu, Appl. Phys. Lett., 2007, 90, 021917.
65 H. E. Kissinger, Anal. Chem., 1957, 29, 1702–1706.
66 H. J. Lin, C. Zhang, H. Wang, L. Z. Ouyang, Y. F. Zhu, L. Q. Li, W. H. Wang and M. Zhu, J. Alloys Compd., 2016, 685, 272–277.
67 M. Q. Fan, S. S. Liu, Y. Zhang, J. Zhang, L. X. Sun and F. Xu, Energy, 2010, 35, 3417–3421.