Microstructure and hydrogen storage kinetics of Mg$_{89}$RE$_{11}$ (RE = Pr, Nd, Sm) binary alloys

Li Chen, Changyi Hu$^a$ and Feng Liu$^b$

The present work reports the fabrication of Mg$_{89}$RE$_{11}$ (RE = Pr, Sm, Nd) alloys by a vacuum induction furnace. The phase analysis, structural characterization and microstructure observation of Mg$_{89}$RE$_{11}$ alloys were carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). There exhibits a multiphase microstructure in the as-cast Mg$_{89}$RE$_{11}$ (RE = Pr, Nd, Sm) alloys from the comprehensive analysis made from XRD and SEM, which are containing the major phase (RE$_3$Mg$_{41}$) and several secondary phases (RE$_2$Mg$_7$ and RE$_2$Mg$_{12}$). The determination of XRD and TEM reveal that these experimental alloys turn into a MgH$_2$ nanocrystalline composite with equably distributed RE hydride nanoparticles after hydriding and this MgH$_2$ major phase turns into a Mg nanocrystalline after dehydriding. The determination results of the hydrogen storage kinetics show that adding the rare earth element (Pr, Sm and Nd) ameliorates the hydriding and dehydriding kinetics of the Mg-based alloys dramatically. The hydrogen desorption activation energy $E_d$(de) of Mg$_{89}$Pr$_{11}$, Mg$_{89}$Nd$_{11}$, Mg$_{89}$Sm$_{11}$ are 140.595, 139.191, 135.280 kJ mol$^{-1}$ H$_2$, respectively. Specially, the hydrogen storage capacity (wt%) of Mg$_{89}$Sm$_{11}$ alloy that added Sm element can reached 5 wt%. The improvement of the hydrogen storage performance of Mg$_{89}$RE$_{11}$ alloys can be principally ascribed to the RE hydride nanoparticles facilitating the hydriding and dehydriding reactions.

Introduction

Mg-based alloys have been widely deemed as attractive hydrogen storage materials for hydrogen fuel cells due to their outstanding advantages including good hydrogen storage capacity, low-cost and high accessibility.$^{1-3}$ However, the application of Mg-based alloys has been hampered by their relatively high dehydrogenation temperature and sluggish hydriding/dehydriding kinetics along.$^{4-7}$ Among the methods to improve the hydriding/dehydriding kinetics, finding effective alloying elements has been one of the most important research focuses for Mg-based alloys.

So far, a variety of chemical elements, such as In,$^{5,7}$ Ni,$^{8-10}$ Zr,$^{11,12}$ Ag,$^{13}$ Al,$^{14,15}$ Ti,$^{16,17}$ rare earth (RE) elements$^{18}$ and their composites,$^{19-23}$ have been exploited as the alloying elements for the Mg-based alloys. Among them, adding RE elements attracts extensive interest for the Mg-based alloys due to its excellent improvement of the hydriding/dehydriding rate, which may be a better choice to meet the requirements of future hydrogen energy storage systems.$^{24-29}$ Therefore, the addition of rare earth elements into Mg-based alloys as alloying elements shed light on the better hydrogen storage properties for alloys. The hydrogen storage capacity of La$_2$Mg$_{17}$ reaches 6 wt% at the temperature of 350 °C.$^{30}$ The Mg$_3$La compound prepared by induction melting can absorb 2.89 wt% of hydrogen reversibly at 296 °C.$^{31}$ Wu et al.$^{32}$ investigated the hydrogen storage properties and phase transitions of Mg$_{17}$Ba$_2$, which has reversible hydrogen capacity of 4.0 wt% H$_2$. Ma et al.$^{33,34}$ proposed the addition of Ni to the CaMg$_2$-based alloys resulted in room-temperature hydrogen absorption without an activation process, and a maximum hydrogen-absorption capacity of 5.65 wt%. Moreover, dual-tuning effects of the thermodynamics and kinetics for Mg-based materials is one of the key issues for hydrogen economy and hydrogen storage materials.$^{35-37}$ Cao et al.$^{38}$ found that the Mg$_{58}$In$_5$Al$_5$Ti$_5$ alloy displays both enhanced dehydriding kinetics and thermodynamics, which is prepared by plasma milling (P-milling).$^{39}$ The addition of In into Mg$_2$Ni not only greatly enhanced the dehydriding kinetics but also significantly lowered the thermodynamic stability.$^{37}$

Although the research of Mg-based hydrogen storage alloys has made much substantial progress, the cost of hydrogen storage alloys has been increased by high alloying element content, and the hydrogen storage performance needs to be further improved. In this work, we report a time-saving vacuum inducing smelting method to synthesize low alloying Mg$_{89}$RE$_{11}$ (RE = Pr, Nd, Sm) binary alloys as new hydrogen storage materials. On the one hand, we evaluated hydrogen storage properties of the Mg$_{89}$RE$_{11}$ (RE = Pr, Nd, Sm) binary alloys. On the other hand, we deeply discussed the hydriding and dehydriding mechanism for the Mg$_{89}$RE$_{11}$ (RE = Pr, Nd, Sm) binary alloys further.
Experimental

The compositions of alloys in this experiment were designed to be Mg$_{89}$RE$_{11}$ (RE = Pr, Nd, Sm). The alloy ingots were melted and synthesized with a certain mass ratio metal by using a vacuum induction furnace. In order to prevent the volatilization and oxidation of magnesium and rare earth elements, 0.04 MPa helium was used as the protection gas in the smelting process. After the liquid alloy is injected into the copper mold, the parent alloy ingot is obtained after cooling.

Some microstructures of the samples, including microscopic morphology, phase composition and crystal structure, were observed and characterized by TEM (JEM-2100F) linked with an SAED (selected area electron diffraction), SEM (FEI Quanta 400) linked with an EDS (Energy Disperse Spectroscopy, EDAX Apollo 40 silicon drift detector). For phase analysis, XRD (D/max/2400) technique was employed.

A series of tests on the kinetics of hydrogen absorption and desorption of alloys were carried out on an automatically controlled Sieverts apparatus. The alloys used in above test need to be mechanically pulverized in advance and the powder between 48–75 μm is screened for testing. The sample weighing 1 g was put into the reaction chamber and repeatedly absorbed/desorbed hydrogen until completely activated. When the initial hydrogen pressure of hydriding process was set at 3 MPa, the hydrogen absorption experiment was carried out in the temperature range of 150–380 °C. At the same temperature, the initial hydrogen pressure in hydrogen desorption was set at 1 × 10$^{-4}$ MPa.

Results and discussion

Microstructure of as-cast Mg$_{89}$RE$_{11}$ (RE = Pr, Nd, Sm) binary alloys

The phase composition and phase structure of the as-cast Mg$_{89}$RE$_{11}$ (RE = Pr, Nd, Sm) binary alloys are shown contrastively in the XRD diagram of Fig. 1. These three alloys have the typical crystalline structure. After the analysis using the Jade 6.0 software on the crystal cell parameters of the phase of as-cast alloys, we could find the as-cast Mg$_{89}$Pr$_{11}$ alloy is composed of major phase Pr$_{5}$Mg$_{41}$ with space group of I4m tetragonal structure (the lattice parameters are showing $a = b = 1.4780$ nm, $c = 1.0430$ nm) and secondary phase PrMg$_{3}$ with space group of Fm3m cubic structure (the lattice parameter is showing $a = 0.7388$ nm) and Pr$_{7}$Mg$_{41}$ with space group of I4mmn tetragonal structure (the lattice parameters are showing $a = b = 1.0340$ nm, $c = 0.5980$ nm). The as-cast Mg$_{89}$Nd$_{11}$ alloy contains major phase Nd$_{3}$Mg$_{41}$ with space group of I4m tetragonal structure (the lattice parameters are showing $a = b = 1.4760$ nm, $c = 1.0390$ nm) and secondary phase Nd$_{2}$H$_{5}$ with space group of Fm3m cubic structure (the lattice parameter is showing $a = 0.7438$ nm) and NdMg$_{3}$ with space group of I4mmn tetragonal structure (the lattice parameters are showing $a = b = 1.0310$ nm, $c = 0.5930$ nm). The as-cast Mg$_{89}$Sm$_{11}$ alloy is made up with two parts, major phase Sm$_{5}$Mg$_{41}$ with space group of I4m tetragonal structure (the lattice parameters are showing $a = b = 1.4815$ nm, $c = 1.0366$ nm) and secondary phase SmMg$_{3}$ with space group of Fm3m cubic structure (the lattice parameter is showing $a = 0.7346$ nm). Unlike the Mg$_{89}$Sm$_{11}$ alloy, both Mg$_{89}$Pr$_{11}$ alloy and Mg$_{89}$Nd$_{11}$ alloy include three different types of phases. The stronger the secondary phase diffraction peaks of Mg$_{89}$Pr$_{11}$ alloy and Mg$_{89}$Nd$_{11}$ alloy express, the higher the secondary phase content will be.

Fig. 2 displays the SEM micrographs of as-cast Mg$_{89}$RE$_{11}$ (RE = Pr, Nd, Sm) binary alloys. Taking as-cast Mg$_{89}$Sm$_{11}$ alloy as an example, the EDS patterns of A and B regions are depicted to represent the alloy content of each region. The two regions with different degrees of darkness in the as-cast alloy represent the two-phase structure of the alloy. The results combining the EDS and XRD analysis show that the white and dark gray areas are SmMg$_{3}$ and Sm$_{3}$Mg$_{11}$, respectively.

Hydriding and dehydriding mechanism

The XRD patterns of the Mg$_{89}$RE$_{11}$ (RE = Pr, Nd, Sm) binary alloys after hydrogen absorption/desorption completely are shown in Fig. 3, all of which alloys display the typical crystalline structure. For Mg$_{89}$Pr$_{11}$ alloy, there are three phases formed after hydrogen absorption, including the major phase MgH$_{2}$ with space group of P4$_{2}$/mmm tetragonal structure (the lattice parameters are showing $a = b = 0.4517$ nm, $c = 0.3020$ nm) and secondary phase PrH$_{2}$ with space group of Fm3m cubic structure (the lattice parameter is showing $a = 0.5486$ nm) and Pr$_{8}$H$_{18.96}$ with space group of I4,md tetragonal structure (the lattice parameters are showing $a = b = 0.5494$ nm, $c = 1.1078$ nm). While after hydrogen desorption, the major phase Mg with space group of P6$_{3}$/mmc hexagonal structure (the lattice parameters are showing $a = b = 0.3209$ nm, $c = 0.1624$ nm) and secondary phase PrH$_{2}$ are existing. With respect to Mg$_{89}$Nd$_{11}$, the major phase MgH$_{2}$ and secondary phase Nd$_{2}$H$_{5}$ with space group of I4,md tetragonal structure (the lattice parameters are showing $a = b = 0.5413$ nm, $c = 1.0870$ nm) exist after hydrogen absorption. And the major phase Mg and secondary phase Nd$_{2}$H$_{5}$ form after hydrogen desorption. With regard to Mg$_{89}$Sm$_{11}$, the major phase MgH$_{2}$ and secondary phase Sm$_{3}$H$_{7}$ with space...
Fig. 2  SEM micrographs and EDS of as-cast samples for Mg89RE11 (RE = Pr, Nd, Sm) alloys: (a) RE = Pr; (b) RE = Nd; (c) RE = Sm.

Fig. 3  XRD spectrum of saturated hydrogenation and fully dehydrogenation samples at 380 °C for Mg89RE11 (RE = Pr, Nd, Sm) alloys: (a) saturated hydrogenation samples; (b) fully dehydrogenation samples.
group of $I4m$ tetragonal structure (the lattice parameters are showing $a = b = 0.3778$ nm, $c = 0.5365$ nm) form after hydrogen absorption. It is the major phase Mg and secondary phase $\text{Sm}_3\text{H}_7$ that are existing after hydrogen desorption. It can be concluded that the hydride $\Pr\text{H}_2$, $\text{Nd}_2\text{H}_5$ and $\text{Sm}_3\text{H}_7$ possess characteristics of good thermal stability at $400 ^\circ\text{C}$.\textsuperscript{38} According to the XRD analysis and literature,\textsuperscript{39} we infer conceivable reaction pathways:

![Fig. 4](image)

**Fig. 4** TEM and HRTEM micrographs and SAED rings of the hydrogen desorption samples for Mg$_{89}$RE$_{11}$ (RE = Pr, Nd, Sm) alloy: (a) RE = Pr; (b) RE = Nd; (c) and (d) RE = Sm.

![Fig. 5](image)

**Fig. 5** Isothermal hydrogen absorption (a) and desorption (b) kinetic curves of Pr$_{11}$Mg$_{89}$ alloy at different temperatures and the corresponding Arrhenius plots (c) and (d).
$\text{Mg}_{89}\text{Pr}_{11} + \text{H}_2 \rightarrow \text{PrH}_2 + \text{Pr}_5\text{H}_{18.96} + \text{MgH}_2$

$\leftrightarrow \text{PrH}_2 + \text{Mg} + \text{H}_2$

$\text{Mg}_{89}\text{Nd}_{11} + \text{H}_2 \rightarrow \text{Nd}_2\text{H}_5 + \text{MgH}_2$

$\leftrightarrow \text{Nd}_2\text{H}_5 + \text{Mg} + \text{H}_2$

$\text{Mg}_{89}\text{Sm}_{11} + \text{H}_2 \rightarrow \text{Sm}_3\text{H}_7 + \text{MgH}_2$

$\leftrightarrow \text{Sm}_3\text{H}_7 + \text{Mg} + \text{H}_2$

The fundamental reason for reversible hydrogen absorption/desorption of the active $\text{Mg}_{89}\text{RE}_{11}$ ($\text{RE} = \text{Pr, Nd, Sm}$) binary alloys is coming from the formation and decomposition of $\text{MgH}_2$.

Fig. 4 shows the TEM and HRTEM micrographs and SAED rings of the fully hydrogen desorption samples at 380 $^\circ$C for $\text{Mg}_{89}\text{RE}_{11}$ ($\text{RE} = \text{Pr, Nd, Sm}$) alloy. According to the inset of Fig. 4(a)–(c), the alloys are composed of the Mg and REH$_x$ (PrH$_2$, Nd$_2$H$_5$ and Sm$_3$H$_7$) nanocrystal phases, which conforms to the XRD detections. As the observation of the internal lattice structure from HRTEM (Fig. 4(d)), the interplanar spacing of Mg nanocrystalline on (100) crystal surface is 0.278 nm and the secondary phase Sm$_3$H$_7$ nanocrystal on (101) crystal surface is 0.309 nm. The hydrogen absorption alloy turns into a Mg nanocrystalline composite with equably distributed Sm$_3$H$_7$ nanoparticles (<100 nm) after dehydriding. The mechanism of the nucleation and growth of the formed REH$_x$ (PrH$_2$, Nd$_2$H$_5$ and Sm$_3$H$_7$) composites is similar to CeH$_{2.73}$–MgH$_2$–Ni composites.$^{39}$ It can be found that the secondary phase PrH$_2$, Pr$_5$H$_{18.96}$, Nd$_2$H$_5$ and Sm$_3$H$_7$ served as catalysts$^{39}$ affect the hydrogen absorption and desorption rates.

**Hydrogen storage kinetics**

For studying the effects of the alloying of Mg with rare earth elements on hydrogen storage kinetics, it is necessary to determine the hydrogen absorption/desorption curves of these $\text{Mg}_{89}\text{RE}_{11}$ ($\text{RE} = \text{Pr, Nd, Sm}$) binary alloys at various temperatures. The Johnson–Mehl–Avrami–Kolmogorov (JMAK) method can be generally applied to model the hydrogen absorption and desorption data, and there is a linear equation expressed following: $^{40}$

$$\ln[-\ln(1 - \alpha)] = \eta \ln k + \eta \ln t$$  \hspace{1cm} (4)

where $\alpha$, $\eta$, $k$ and $t$ are the percentage of Mg converted to MgH$_2$, the Avrami exponent reaction order, the kinetic parameter and the time, respectively. Based on some experimental data have been measured, we are able to draw the fitting linear plots of $\ln[-\ln(1 - \alpha)]$ vs. $\ln t$ and obtain the $\eta$ and $\eta \ln k$ values at various temperatures lightly from the slope and intercept of above plots. As a result, the rate constant $k$ will be figured out expeditiously using eqn (4). Thus, by means of introducing the $k$ values into the following Arrhenius equation, we will calculate the apparent activation energy ($E_a$) for the absorption and desorption process logically:$^{41}$

$$k = A \exp[-E_a/RT]$$  \hspace{1cm} (5)

where $A$, $R$ and $T$ are the temperature independent coefficient, the universal gas constant (8.3145 J K$^{-1}$ mol$^{-1}$), and the absolute Kelvin temperature, respectively.
Fig. 5(a) shows the hydrogen absorption curves of the Mg89Pr11 alloy, which were measured at 150 to 380 °C under the initial hydrogen pressure of 3 MPa. The increase of hydrogen absorption capacity will bring with the increase of the temperature for the alloy. It can be suggested that increasing temperature facilitates the improvement of the hydriding kinetics of the alloy. In terms of specific data, the hydrogen absorption capacity of 3.712 wt% for the alloy can be reached within 10 min at 250 °C, compared to only 2.4 wt% for pure MgH2 even if it lasts 20 min and under the same condition. Fig. 5(b) displays the hydrogen desorption curves of the Mg89Pr11 alloy, which were measured at 300 to 360 °C under 1 x 10^-4 MPa pressure. The final hydrogen desorption capacity of 4.7 wt% for this alloy is lower than own hydrogen absorption capacity due to the lower final hydrogen pressure (<1 x 10^-2 MPa) of the test system. The hydrogen desorption of the hydrogenated alloy at 320 °C, 340 °C and 360 °C have finished within 8235 s, 3420 s and 1890 s, respectively. Unlike no decomposition for the milled MgH2 at 300 °C, 3.45 wt% H for the Mg89Nd11 alloy is desorbed in 200 min. Fig. 5(c) and (d) illustrate the Arrhenius plot of ln k vs. 1000/RT under hydrogenation and dehydrogenation conditions, respectively. The calculated activation energy for the hydrogenation (Ea(ab) = 90.35 kJ mol^-1) is much lower than that of Mg powder after cyclic activation process (100 kJ mol^-1).44 For the dehydrogenation, the values of activation energy are 160 and 156 kJ mol^-1 for un-milled MgH2 (ref. 44 and 45) and the value of which is 158.5 kJ mol^-1 for pure milled MgH2, which values all show larger than the calculated Ea(de) value (140.60 kJ mol^-1) for the Mg89Pr11 alloy.

In the initial pressure in the 3 Mpa, the hydrogen absorption curves of the Mg89Nd11 alloy tested at temperatures ranging from 150 to 380 °C are displayed in Fig. 6(a). The hydrogen absorption capacity of the alloy increases from 2.403 wt% at 150 °C to 4.491 wt% at 380 °C. It can be found that the increase of the temperature facilitates the improvement of the hydriding kinetics of the alloy. Under the condition of 250 °C, the hydrogen absorption capacity of 3.712 wt% for the alloy could reach within 10 min. Fig. 6(b) exhibits the hydrogen desorption curves of the Mg89Nd11 alloy measured at 300 to 360 °C under 1 x 10^-4 MPa pressure. The final hydrogen desorption capacity of 4.7 wt% for the alloy is also lower than the hydrogen absorption capacity. The hydrogen desorption of the hydrogenated alloy at 320 °C, 340 °C and 360 °C have finished within 8235 s, 3420 s and 1890 s, respectively. Unlike no decomposition for the milled MgH2 at 300 °C, 3.45 wt% H for the Mg89Nd11 alloy is desorbed in 200 min. Fig. 6(c) and (d) illustrate the Arrhenius plot of ln k vs. 1000/RT that is able to reflect the hydrogenation and dehydrogenation kinetics of the Mg89Nd11 alloy. The calculated Ea(ab) value (84.072 kJ mol^-1) is also much lower than that of Mg powder (100 kJ mol^-1). For the dehydrogenation, the Ea(de) value from calculating is 139.193 kJ mol^-1 approximately.

The hydrogen absorption curves of the Mg89Sm11 alloy, which were measured at 150 to 380 °C under 3 MPa hydrogen pressure, shows in Fig. 7(a). The hydrogen absorption capacity of the alloy increases from 2.803 wt% at 150 °C to 5.022 wt% at 380 °C, suggesting that the increasing temperature promotes the improvement of the hydriding kinetics. The hydrogen absorption capacity of 4.112 wt% for the alloy can achieve within 10 min at 250 °C. The hydrogen desorption curves of the

![Fig. 7](image-url)
Mg$_{89}$Sm$_{11}$ alloy tested at 300 to 360 °C under 1 × 10$^{-3}$ MPa are depicted in Fig. 7(b). The final hydrogen desorption capacity of 5.0 wt% for the alloy is lower than the hydrogen absorption capacity. Length of time for the completion of hydrogen desorption of the hydrogenated alloy at 320 °C, 340 °C and 360 °C have finished within 6556 s, 2527 s and 1106 s, respectively. Compared to no decomposition for the milled MgH$_2$ at 300 °C, 3.572 wt% H for the Mg$_{89}$Sm$_{11}$ alloy is desorbed in 200 min. The Arrhenius plot of ln $k$ vs. 1000/RT for the hydrogenation and dehydrogenation kinetics are displayed in Fig. 7(c) and (d). The calculated $E_a$(ab) and $E_a$(de) values are about 77.802 kJ mol$^{-1}$ 135.280 kJ mol$^{-1}$, respectively.

Synthesizing the above analysis, the hydrogen storage kinetics properties of Mg$_{89}$RE$_{11}$ (RE = Pr, Nd, Sm) alloys are listed in the Table 1. For Mg$_{89}$RE$_{11}$ (RE = Pr, Nd, Sm) alloys, the order of hydrogen absorption and desorption rate is Sm > Nd > Pr. However, the apparent activation energy ($E_a$) both absorption and desorption course are all decreased, and the order is Sm < Nd < Pr. It can be concluded that the Mg$_{89}$Sm$_{11}$ alloy is the highest hydrogen storage kinetics properties alloy. The results shows that the hydrogen sorption properties of Mg-based alloys can be substantially improved by forming composites having catalytic effect and proper microstructure features.47–49

**Table 1** Hydrogen storage kinetics properties of Mg$_{89}$RE$_{11}$ alloys

| Mg$_{89}$RE$_{11}$ alloy | 250 °C, capacity within 10 min (wt%) | 320 °C, complete dehydrogenation time (s) | $E_a$(ab) kJ mol$^{-1}$ | $E_a$(de) kJ mol$^{-1}$ |
|------------------------|-------------------------------------|----------------------------------------|-----------------|-----------------|
| RE = Pr                | 3.712                                | 10 350                                 | 90.35           | 140.60          |
| RE = Nd                | 3.895                                | 8235                                  | 84.07           | 139.19          |
| RE = Sm                | 4.112                                | 6556                                  | 77.802          | 135.28          |
| MgH$_2$ (ref. 42–45)   | 2.4 wt%                               | Stable                                 | 100             | 156/160         |

**Conclusions**

In summary, Mg$_{89}$RE$_{11}$ (RE = Pr, Nd, Sm) alloys can be synthesized via a time-saving vacuum inducing smelting approach. The conclusions drawn from this work is sketched as blowes:

1. The as-cast Mg$_{89}$RE$_{11}$ (RE = Pr, Nd, Sm) alloy contains a major phase RE$_3$Mg$_{41}$ (RE = Pr, Nd, Sm) as well as two kinds of secondary phase REMg$_5$ (RE = Pr, Nd, Sm) or REMg$_{12}$ (RE = Pr, Nd). After hydrogen absorption, there will form a major phase MgH$_2$ and a secondary phase PrH$_2$ and PrH$_{18.96}$ for RE = Pr, Nd, H$_2$ for RE = Nd, Sm, H$_2$ for RE = Sm. After hydrogen desorption, there will exist the major phase Mg and a secondary phase PrH$_2$ for RE = Pr, Nd, H$_2$ for RE = Nd, Sm, H$_2$ for RE = Nd.

2. The RE hydrides (PrH$_2$, NdH$_2$, and SmH$_2$) are equably distributed in the MgH$_2$ nanocrystalline phase and possess characteristics of good thermal stability. These RE hydrides (<100 nm) served as catalysts increase the hydrogen absorption and desorption rates. In these three kinds of hydrogen storage alloys, the Mg$_{89}$Sm$_{11}$ alloy shows the lowest apparent activation energy both in the absorption and desorption and the fastest hydrogen absorption and desorption rates.

**Conflicts of interest**

There are no conflicts to declare.

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