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Hydrogen storage properties of Mg–Ce–Ni nanocomposite induced from amorphous precursor with the highest Mg content

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ABSTRACT

The effect of Ce and Ni contents on the glass-forming ability (GFA) of Mg–Ce–Ni system in the Mg-rich corner of Mg–Ce–Ni system is revealed. Ce is more advantageous for the GFA of Mg-rich Mg–Ce–Ni system than Ni, and the lowest Ce content is ~5 at.% to obtain the fully amorphous alloy. Amorphous alloy with the highest Mg content, $Mg_{90}Ce_5Ni_5$, was obtained by melt-spinning. With the amorphous alloy as precursor, nanostructure multiphases compositae was prepared by crystallizing it in hydrogenation process. The compositae with reversible hydrogen storage capacity of 5.3 wt.% shows much faster kinetics and lower MgH₂ desorption activation energy than those of induction-melt $Mg_{90}Ce_5Ni_5$ alloy. Both in situ formed nanosized Mg_2Ni and $CeH_{2.73}$ act as effective catalysts and significantly improve the hydrogen storage properties of MgH_2 .

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1. Introduction

Hydrogen storage is the key issue to realize the hydrogen economy [1,2]. And among the hydrogen storage materials family, Mg-based alloys are a group of promising candidates mainly due to their high hydrogen storage capacity, e.g., 7.6 wt.% in the case of MgH₂, low cost and abundant resources [3]. However, they suffer from kinetic and thermodynamic drawbacks on their way to practical application, which are characterized by high activation energy (~160 kJ/mol) and enthalpy (~75 kJ/mol H₂) for MgH₂ desorption [4,5]. Although great efforts have been made to overcome those drawbacks through catalysing [5,6], nanostructuring [7] and alloying [8,9] etc., the performance of Mg-based alloys is still far behind the

on-board application requirements. It seems that no simple sole method could solve the problem and strategy of interdisciplinary approach should be explored to tune both hydrogen storage kinetics and thermodynamics of them.

Since the last decades, extensive efforts have been made to modify Mg-rich Mg–RE–Ni (RE = Rare earth) alloys by rapid solidification, and amorphous and/or nanocrystalline structures are usually resulted in [10–19]. Spassov et al. [10–12] reported that some nanocrystalline and/or amorphous Mg–RE–Ni alloys showed much superior hydrogen absorption/desorption properties than the corresponding conventional crystalline alloys. Wu et al. [14,20,21] studied the effect of solidification rate on the microstructures and hydrogen storage properties of melt-spun Mg–Ni–Mm (Mm = La,

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Ce-rich Mishmetal) alloy and found that the hydrogenation properties showed close connection with the microstructures; the refined microstructure was very beneficial to the hydrogen storage properties of Mg-based materials. Zhang et al. [16] prepared a melt-spun Mg-Y-Ni alloy with a long-period stacking ordered (LPSO) phase, the nanostructured YH₂ (or YH₃) and Mg₂Ni significantly improve the hydrogen storage properties of MgH₂. The improvement on absorption kinetics for Mg-based materials can be attributed to the nanosized particles of REH_x and Mg₂Ni which embedded in Mg matrix after activation, while the enhancement of desorption kinetics to the nanosized particles of REH_x and Mg₂NiH₄ embedded in MgH₂ matrix upon hydrogenation. It should be pointed out that the in situ formation of nanocrystalline REH_x and Mg₂Ni (or Mg₂NiH₄) particles are important for abovementioned enhancement in Mg-RE-Ni system. From literatures [14,19,22] and our previous work [17], the more homogeneous precursor, the better hydrogen storage properties, and thus amorphous structure is the most expected.

The contents of RE and Ni are very important to Mg-RE-Ni hydrogen storage alloys. On one hand, RE and Ni are advantageous elements for the GFA of Mg-based alloys and the hydrogen storage properties of MgH₂. On the other hand, Ni and RE are much heavier than Mg, which reduces the hydrogen storage capacity for Mg-based alloys. It is not easy to get the fully amorphous Mg-RE-Ni alloys with Mg content of \sim 90 at.% [23]. Thus, Ni and RE contents should be designed in a reasonable range by considering the requirement of hydrogen storage capacity and GFA to make use of in situ formed nanocomposite from amorphous precursor to improve hydrogen storage properties of Mg-based materials. Till now, no systematical work has been done on the effect of RE and Ni contents on the GFA for Mg-rich Mg-RE-Ni system, and it is worthy to reveal such effect to design materials reasonably. Very recently, we found that Mg–Ce–Ni system showed very good GFA with record high Mg content of 90 at.% [24]. The high Mg content is suitable to test the effect of Ce and Ni contents on the GFA of Mg-Ce-Ni system in the Mg-rich corner.

In the present study, we focus on the effect of Ce and Ni contents on the GFA of Mg–Ce–Ni system in Mg-rich corner of Mg–Ce–Ni phase diagram. Because the hydrogen storage kinetics is not much influenced by different REH_x for melt-spun Mg–RE–Ni alloys [19]. Our present work can also be reference for design of other Mg–RE–Ni hydrogen storage alloys. Moreover, hydrogen storage properties of amorphous Mg–Ce–Ni alloy with the highest Mg content are studied in detail.

2. Experimental details

CeNi, CeNi₂, CeNi₃ and Ce₅Ni₄ intermediate alloys were firstly fabricated by arc-melting. Mg–Ce–Ni ingots (including Mg₈₈Ce₄Ni₈, Mg₈₈Ce₃Ni₉, Mg₉₀Ce₅Ni₅, Mg₉₁Ce₅Ni₄, Mg₉₂Ce₄Ni₄ and Mg₉₄Ce₃Ni₃) were then prepared by conventional induction-melting of a mixture of Ce–Ni intermediate alloys and pure Mg metal in a quartz crucible under argon atmosphere. Subsequently, the ingots were all re-melted and injected through a nozzle ($\phi = 1$ mm) onto the surface of



Fig. 1 – XRD patterns of melt-spun (a) $Mg_{88}Ce_4Ni_8$, (b) $Mg_{88}Ce_3Ni_9$, (c) $Mg_{90}Ce_5Ni_5$, (d) $Mg_{91}Ce_5Ni_4$, (e) $Mg_{92}Ce_4Ni_4$ and (f) $Mg_{92}Ce_3Ni_3$ alloys.

a rotating copper wheel at a linear velocity of 30 m/s. The Mg–Ce–Ni ribbons of ~2.5 mm in width and ~40 μm in depth were obtained after melt spinning.

Phase structure analyses were characterized by a Philips X'Pert MPD X-ray diffractometer (XRD) equipped with Cu K α radiation. Morphologies of the dehydrogenated samples were examined by back-scatting scanning electron microscopy (SEM, ZEISS SUPAR 40/VP). Crystallization experiment was performed using a Perkin Elmer differential scanning calorimeter (DSC) at a heating rate of 10 K/min. Thermal desorption spectroscopy (TDS) was performed using an NETZSCH DSC equipment at different heating rates.

Prior to hydrogen storage property measurements, the melt-spun ribbons were ball milled into powders for only



Fig. 2 – DSC traces of melt-spun (a) $Mg_{88}Ce_4Ni_8$, (b) $Mg_{88}Ce_3Ni_9$, (c) $Mg_{90}Ce_5Ni_5$, (d) $Mg_{91}Ce_5Ni_4$, (e) $Mg_{92}Ce_4Ni_4$ and (f) $Mg_{94}Ce_3Ni_3$ alloys. Melt-spun $Mg_{88}Ce_3Ni_9$ and $Mg_{94}Ce_3Ni_3$ alloys show no peak, indicating their crystalline structures.



Fig. 3 – GFR of the Mg–Ce–Ni system in the Mg-rich corner. In the amorphous Mg–Ce–Ni system, $Mg_{90}Ce_5Ni_5$ alloy owns the highest Mg content and the lowest Ce content.

30 min. Hydrogen storage property measurements were performed on a Sieverts-type automatic gas reaction controller (Pct Pro2000). The sample weights for hydrogen storage property measurements of induction-melt and melt-spun Mg₉₀Ce₅Ni₅ alloys are 0.329 g and 0.227 g, respectively.

3. Results and discussions

GFA of Mg–Ce–Ni system in the Mg-rich corner

Fig. 1 shows the XRD patterns of melt-spun Mg–Ce–Ni alloys. Melt-spun Mg₈₈Ce₄Ni₈ alloy shows Mg and amorphous peak while melt-spun Mg₈₈Ce₃Ni₉ alloy consists of Mg, Ce₂Mg₁₇ and a Long-Period Stacking Order (LPSO) phase which matches the XRD patterns of melt-spun Mg–Y–Ni alloy in Zhang's study [16]. From XRD patterns and TEM analysis published elsewhere [24], melt-spun Mg₉₀Ce₅Ni₅ alloy are fully amorphous while melt-spun Mg₉₂Ce₄Ni₄ is nanocrystalline Mg embedded in an amorphous matrix. Melt-spun Mg₉₁Ce₅Ni₄ alloy consists of Mg phase and an amorphous broad peak. Melt-spun Mg₉₄Ce₃Ni₃ alloy consists of Mg, Ce₂Mg₁₇ and Mg₂Ni phases.

Crystallization processes of melt-spun Mg–Ce–Ni alloys are revealed by DSC measurements as shown in Fig. 2. Meltspun $Mg_{94}Ce_3Ni_3$ and $Mg_{88}Ce_3Ni_9$ alloys display no peaks, indicating they are fully crystalline, which suggests that the GFA of Mg–Ce–Ni system deteriorates drastically if Ce content is as low as 3 at.%. Once Ce content reached 4 at.%, melt-spun Mg–Ce–Ni alloys easily became partially amorphous, and 5 at.% of Ce can obtain fully amorphous structure. Obviously, Ce content is more important to GFA of Mg–Ce–Ni system in the Mg-rich corner than that of Ni content. Along with some results reported in Ref. [23], the glass-forming range (GFR) of Mg–Ce–Ni system in the Mg-rich corner is summarized in Fig. 3. Herein, crystallization products of the melt-spun Mg–Ce–Ni alloys are also studied by XRD (results not shown), and the DSC peaks and crystallization products are summarized in Table 1.

The GFR is very useful for materials design for the Mg–RE–Ni hydrogen storage alloys. In the amorphous Mg–Ce–Ni system, $Mg_{90}Ce_5Ni_5$ alloy owns the highest Mg content and the lowest Ce content, which are advantageous for both hydrogen storage capacity and kinetics. Herein, the authors take the amorphous $Mg_{90}Ce_5Ni_5$ alloy as precursor to induce nanophase composite for hydrogen storage, and the hydrogen storage properties via precise materials design are studied.

3.2. Phase transition of the amorphous $Mg_{90}Ce_5Ni_5$ alloy

As shown in Table 1, after fully crystallization until 573 K, melt-spun $Mg_{90}Ce_5Ni_5$ alloy is decomposed into Ce_2Mg_{17} , Mg, Mg₂Ni and Mg₆Ni phases. Fig. 4 shows the XRD patterns of hydrogenation and dehydrogenation products of the crystallized melt-spun Mg₉₀Ce₅Ni₅ alloy after 10 hydrogenation/ dehydrogenation cycles at 573 K. Hydrogenation products are MgH₂, Mg₂NiH₄ and CeH_{2.73} while dehydrogenation products are Mg, Mg₂Ni and CeH_{2.73}. As it is known, Mg and Mg₂Ni uptake and release hydrogen reversibly, while Ce2Mg17 undertakes disproportion reaction upon the first hydrogenation and decomposed into MgH₂ and CeH_{2.73}. Mg₆Ni is a metastable phase [25] and it decomposed into Mg₂NiH₄ and MgH₂ upon hydrogenation. CeH_{2.73} stays stable in hydrogen absorption/desorption cycles, indicating it is not like YH₃, which can decompose into YH2 after dehydrogenation and recovered after hydrogenation under the similar conditions [16]. The grain sizes of Mg and CeH_{2.73} for melt-spun Mg₉₀Ce₅Ni₅ alloy after dehydrogenation are calculated by the Rietveld refinement which is described detailed elsewhere [16,26], and it is found that the average sizes for Mg and CeH_{2.73} are 127.1 nm and 45.3 nm, respectively. The fine

Table 1 – State and crystallization processes of melt-spun Mg–Ce–Ni alloys.					
Chemical composition	Melt-spun state	Crystallization temperature (K)		Crystallization products	
		T _{x1}	T _{x2}	P ₁	P ₂
Mg ₈₈ Ce ₄ Ni ₈	Nano-Mg + amorphous	440/470	513	Mg/Ce ₂ Mg ₁₇	Mg ₂ Ni
Mg ₈₈ Ce ₃ Ni ₉	Crystalline	-	-	-	-
Mg ₉₀ Ce ₅ Ni ₅	Amorphous	455	496	Mg, Ce ₂ Mg ₁₇	Mg ₂ Ni, Mg ₆ Ni
Mg ₉₁ Ce ₅ Ni ₄	Nano-Mg $+$ amorphous	453/492	529	Mg, Ce ₂ Mg ₁₇	Mg ₂ Ni
Mg ₉₂ Ce ₄ Ni ₄	Nano-Mg $+$ amorphous	455	503	Mg, Ce ₂ Mg ₁₇	Mg ₂ Ni
$Mg_{94}Ce_3Ni_3$	Crystalline	-	-	-	-



Fig. 4 - XRD patterns of melt-spun $Mg_{90} Ge_5 Ni_5$ alloy after (a) dehydrogenation and (b) hydrogenation.

particles are good for the catalytic process and hydrogen diffusion. From the XRD results, we conclude the first hydrogenation and hydrogenation/dehydrogenation cycles of melt-spun $Mg_{90}Ce_5Ni_5$ alloy as follows:

1st. hydrogenation: $Ce_2Mg_{17} + H_2 \rightarrow MgH_2 + CeH_{2.73}$

 $Mg + H_2 \rightarrow MgH_2$

 $Mg_2Ni + H_2 \rightarrow Mg_2NiH_4$

 $Mg_6Ni + H_2 \rightarrow Mg_2NiH_4 + MgH_2$

Hy/dehy- Cycles: Mg + H₂ \leftrightarrow MgH₂

 $Mg_2Ni + H_2 \leftrightarrow Mg_2NiH_4$

Morphologies of dehydrogenation products for inductionmelt and melt-spun $Mg_{90}Ce_5Ni_5$ alloys are shown in Fig. 5. Dehydrogenation products for induction-melt $Mg_{90}Ce_5Ni_5$ alloy consists of two typical morphologies, which are magnified in Fig. 5 b and c. Very fine $CeH_{2.73}$ and Mg_2Ni particles are separated out along the Mg bulks of ~ 50 µm in size. However, for the desorbed melt-spun alloy, very fine $CeH_{2.73}$ and Mg_2Ni particles are dispersively embedded in Mg matrix (Fig. 5d). Furthermore, the grain size of Mg from melt-spun alloy is much smaller than that from induction-melt one. The meltspun alloy with elements homogeneously distributed and fully amorphous is advantageous to prepare nanosize Mg with dispersive catalytic Mg_2Ni and $CeH_{2.73}$, which is beneficial for the hydrogen storage properties of Mg.

3.3. Hydrogen storage kinetics of induction-melt and melt-spun $Mg_{90}Ce_5Ni_5$ alloys

Fig. 6a shows the hydrogen absorption kinetics of melt-spun $Mg_{90}Ce_5Ni_5$ alloy under initial pressure of 2.5 MPa. The meltspun alloy displays very rapid hydrogenation kinetics. At 573 K, about 5.0 wt.%-H was absorbed within 5 min, reacting rate of 1 wt.%-H/min, which is faster than that of the meltspun Mg_{12} YNi alloy with a LPSO phase [16]. Fig. 6b compares the hydrogen desorption kinetics for melt-spun and induction-melt $Mg_{90}Ce_5Ni_5$ alloys at 473 and 513 K, all against



Fig. 5 – Back-scatting SEM images of dehydrogenation products of induction-melt (a–c) and melt-spun (d–e) $Mg_{90}Ce_5Ni_5$ alloys.



Fig. 6 – (a) Hydrogen absorption kinetic curves of meltspun Mg₉₀Ce₅Ni₅ alloy. (b) Comparison of the hydrogen desorption kinetic curves of melt-spun and induction-melt Mg₉₀Ce₅Ni₅ alloys at 473 and 513 K, initial state vacuum.

an initial state of vacuum. The melt-spun alloy exhibits much faster kinetics than the induction-melt one; it releases 4.1 wt.%-H within 10 min even at 513 K. In Zhang's study, the melt-spun Mg₁₂YNi alloy desorbed only 2 wt.%-H in 10 min at 523 K [16]. From literatures, the more Mg means the more hydrogenation capacity, but at the expense of kinetic deterioration [27]. However, we can obtain decent hydrogen storage properties through reasonable alloying and efficient processing and avoid the capacity loss to less than 5 wt.%-H.

Fig. 7a displays the TDS spectra of melt-spun and induction-melt $Mg_{90}Ce_5Ni_5$ alloys. The peaks for Mg_2NiH_4 at about 513 K are too small to be distinguished due to the small amount of Mg_2NiH_4 . The main desorption peaks are attributed to MgH_2 desorption. Hydrogen desorption onset temperatures of the melt-spun alloy are ~50 K faster than those of the induction-melt alloy. The relationships between the heating rate and peak temperature for the melt-spun and induction-melt alloys are plotted in Fig. 7b, which fit Kissinger's equation well:

$$\ln\left(\frac{\beta}{T_{\rm m}^2}\right) = -\frac{E_{\rm des}}{RT_{\rm m}} + C \tag{1}$$



Fig. 7 – (a) TDS spectra of induction-melt (black lines) and melt-spun (red lines) $Mg_{90}Ce_5Ni_5$ alloys at different heating rates. (b) Kissinger's plots of MgH_2 desorption processes of melt-spun and induction-melt $Mg_{90}Ce_5Ni_5$ alloys. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

where E_{des} is the activation energy for desorption, T_m is the peak temperature, β is the heating rate, R is gas constant and C is constant. The activation energy of MgH₂ desorption for melt-spun and induction-melt Mg₉₀Ce₅Ni₅ alloys are calculated to be 109.2 and 124.6 kJ/mol, which are much smaller than that of pure MgH₂ of ~ 160 kJ/mol [5]. Alloying Mg with Ce and Ni by induction-melting can reduce the MgH₂ desorption activation energy because Ce and Ni introduction as catalysts reduce the energy barrier for MgH₂ desorption [28]. Melt



Fig. 8 – Desorption PCI curves of induction-melt and meltspun $Mg_{90}Ce_5Ni_5$ alloys at different temperatures.

spinning treatment causes an amorphous precursor with elements homogeneously distributed and grain size reduction, result in an even smaller desorption activation energy.

3.4. PCI properties of the induction-melt and the meltspun $Mg_{90}Ce_5Ni_5$ alloys

Fig. 8 compares the Pressure–Composition Isotherms (PCI) curves for melt-spun and induction-melt $Mg_{90}Ce_5Ni_5$ alloys at different temperatures. Reversible hydrogen storage capacities of the two alloys are both around 5.3 wt.%-H. Considering the XRD patterns of the de/hydrides together, the single plateau should be assigned to Mg-MgH₂ and the hydrogen storage capacity of $Mg_2Ni-Mg_2NiH_4$ is too narrow to be distinguished. Moreover, enthalpy and entropy of MgH_2 desorption, as calculated by Von't Hoff equation, are 74.5 kJ/ mol H₂ and 133.8 J/mol for induction melted alloy, and 77.9 kJ/ mol H₂ and 139.7 J/mol for melt-spun alloy. The equilibrium pressures at 1 atm for the two alloys are both ~557 K. The results are in a very good agreement with the values found in the literature [4,29], indicating that the thermodynamic of $Mg_{90}Ce_5Ni_5$ alloy is not changed by melt-spinning.

4. Conclusions

In summary, the effect of Ce and Ni contents on the GFA of Mg–Ce–Ni system in the Mg-rich corner is studied. Ce is more beneficial for the GFA for the Mg-rich Mg–Ce–Ni system than Ni and the lowest Ce content is ~5 at.% to obtain fully glassy alloy.

 $Mg_{90}Ce_5Ni_5$ with ultrahigh Mg content of 90 at.% can provide the hydrogen storage capacity of more than 5 wt.%, and melt-spinning treatment results in an amorphous precursor with elements homogeneously distributed. The amorphous precursor transforms to nanocomposite constituted of Mg, Mg_2Ni and $CeH_{2.73}$, which are beneficial for synergetic and catalytic process. Moreover, the grains sizes of Mg from amorphous precursor are much smaller than those from conventional crystalline alloy, which shorten the hydrogen diffusion path. These reduces the desorption activation energy to 109.2 kJ/mol, which are much smaller than that of pure MgH₂ of ~160 kJ/mol. Our findings show that strategy of interdisciplinary approach and precise materials design can significantly tune the hydrogen storage properties of Mg-based alloys.

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