



Improved hydrogen absorption and desorption kinetics of magnesium-based alloy via addition of yttrium

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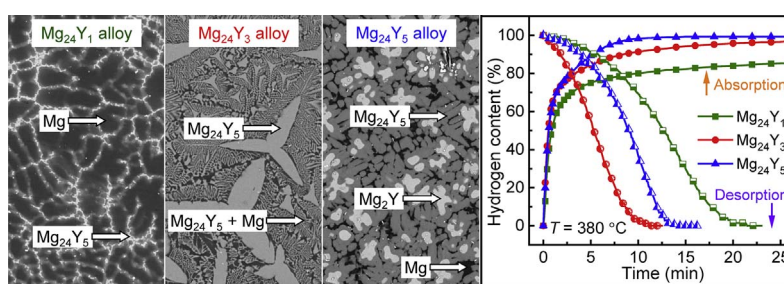
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HIGHLIGHTS

- In situ formed YH₂ nano-particles are observed in hydrogenated Mg–Y alloy.
- Increasing Y content clearly enhances the hydrogen absorption kinetics.
- Mg₂₄Y₃ alloy has the lowest dehydrogenation activation energy (119 kJ mol⁻¹).
- Fine eutectic structure is beneficial to enhance the hydrogen desorption kinetics.

GRAPHICAL ABSTRACT



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ABSTRACT

Yttrium (Y) is selected to modify the microstructure of magnesium (Mg) to improve the hydrogen storage performance. Thereby, binary alloys with the nominal compositions of Mg₂₄Y_x (x = 1–5) are fabricated by inexpensive casting technique. Their microstructure and phase transformation during hydriding and dehydriding process are characterized by using X-ray diffraction, scanning electron microscopy, and high-resolution transmission electron microscopy analysis. The isothermal hydrogen absorption and desorption kinetics are also measured by a Sievert's-type apparatus at various temperatures. Typical multiphase structures of binary alloy can be clearly observed. All of these alloys can reversibly absorb and desorb large amount of hydrogen at proper temperatures. The addition of Y markedly promotes the hydrogen absorption kinetics. However, it results in a reduction of reversible hydrogen storage capacity. A maximum value of dehydrogenation rate is observed with the increase of Y content. The Mg₂₄Y₃ alloy has the optimal desorption kinetic performance, and it can desorb about 5.4 wt% of hydrogen at 380 °C within 12 min. Combining Johnson–Mehl–Avrami kinetic model and Arrhenius equation, the dehydrogenation activation energy of the alloys are evaluated. The Mg₂₄Y₃ alloy also has the lowest dehydrogenation activation energy (119 kJ mol⁻¹).

1. Introduction

In the last decades hydrogen has attracted worldwide interest as ideal energy carrier due to it being a clean energy, most abundant

element in the universe, the lightest fuel and richest in energy per unit mass [1–4]. Safe and efficient hydrogen storage method is a key technology for the advancement of hydrogen and fuel cell power technologies in transportation, stationary, and portable applications [5–8].

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Conventional physical methods, such as compression or liquefaction, have the inherent problems of low volumetric energy density, high economic costs and poor safety issues [9,10]. Another option, chemical hydrogen storage in hydrogen-rich liquids and solids, could potentially achieve high energy storage densities [11,12]. Examples of the solid materials and liquids in this category include boron-based compounds, such as LiBH_4 [13,14], NaBH_4 [13,15] and NH_3BH_3 [13,16,17], and organic liquids, such as cyclohexane, carbazole and decalin [11,18]. However, the non-reversible nature of these hydrogen stores means that it is not a viable hydrogen storage method. The study on physical hydrogen storage in carbon materials, such as activated carbons [19–21], carbon nanotubes [22,23], graphene [24–26], and carbon nanofibers [20,27], is also an active area of research. However, the hydrogen storage capacity of these carbon materials exclusively relies on the external hydrogen pressures and temperature [19]. Metal hydrides also have been considered as a promising candidate for hydrogen storage material because of its high energy density and high security [8,13,28,29]. It is a solid state hydrogen storage method, which can reversibly absorb hydrogen in atomic form and chemically compress hydrogen to high storage densities without high pressure (generally below 3 MPa) [13,30–33]. For instance, typical LaNi_5 -based hydrides can reversibly uptake and release about 0.9 wt% of hydrogen at 100 °C [13]. TiFe alloy has a higher hydrogen storage capacity (less than 2 wt %) [34,35]. However, it suffers from harsh activation procedure and poor absorption/desorption kinetics [34,35]. Mg_2NiH_4 also has the hydrogen storage capacity to release about 3.6 wt% of pure hydrogen [36]. Magnesium hydride, MgH_2 , has the highest energy density of all reversible metal hydrides applicable for hydrogen storage [28]. MgH_2 meets many of the technological demands, such as lightweight, low cost, and considerable gravimetric hydrogen storage capacity (7.6 wt% for MgH_2) [37,38]. However, the sluggish hydriding/dehydriding kinetics and high reaction temperature do not satisfy the requirements for on-board hydrogen supply equipments [39,40].

Alloying of Mg with transition metals (TM), such as Pd, Ni, Nb, Ti, Cu, Zr and V, has shown improvement in hydrogen absorption and desorption kinetics by reducing the activation energy [41–43]. This can be ascribed to the fact that the TM acts as a catalyst to break up the H_2 molecule into absorbable monatomic hydrogen [44]. It was also reported that the intermetallic compounds composed of Mg and rare earth elements (RE) shown an enhanced hydrogen storage properties [45,46]. Poletaev et al. [47] prepared LaMg_{12} alloy by rapid solidification technique, fine lamellar morphology eutectic microstructure was obtained. $\text{La}_2(\text{Mg}, \text{Pd})_{17}$ ternary alloy also shown a multiphase structure, and could absorb about 5 wt% hydrogen at 270 °C within 60 min [48]. Yuan et al. [46] found that $\text{Sm}_5\text{Mg}_{41}$ alloy could reversibly absorb more than 5 wt% of hydrogen at 340 °C, and desorb them within 10 min at the same temperature. Further enhancement of hydrogen sorption kinetics was achieved through the joint addition of RE and Ni [49,50]. Ouyang et al. [51,52] reported that the in situ formed nano $\text{CeH}_{2.73}$ and Ni particles showed a synergetic effect on improving the dehydrogenation kinetic properties of Mg/MgH_2 , which is responsible for the $\text{CeH}_{2.73}$ acts as active nucleation sites for magnesium hydride. Mg_3RE alloys could even absorb hydrogen at room temperature, however, their reversible hydrogen capacity was lower than 3 wt% [53].

Y also belongs to RE elements, which is located in the fifth cycle and IIIB group in the periodic table of elements, and has an atomic number of 39. Compared with other RE elements (such as La, Ce, Pr, Nd, Sm, et al.), Y has a smaller relative atomic mass (88.9). That is to say, the Mg–Y alloy can have higher hydrogen absorption capacity than other Mg–RE (RE = La, Ce, Pr, Nd, Sm, et al.) alloys. Studies on using Y as a catalyst to improve the de/hydrogenation of Mg have also been reported before [54–56]. Improved hydrogen storage kinetics was observed in intermetallic Mg_{24}Y_5 , which is mainly attributed to the modification of microstructures [54,57]. In addition, Mg–Y–TM (TM = Ni, Cu, Ti, Fe, et al.) ternary or quaternary alloy exhibits better hydrogen storage performance [58–60]. However, the effect of Y

content on the hydrogen storage properties of Mg-based alloy remains unknown.

In the present study, the microstructure and hydrogen storage performance of Mg–Y alloys with different Y content were investigated in detail. Aim of this work is to determine the optimized quantity of Y addition, and furthermore, to discuss the phase transformation and relationships between microstructural change and hydrogen storage kinetics of Mg–Y binary alloys.

2. Experimental details

2.1. Preparation of Mg–Y alloys

The Mg_{24}Y_x ($x = 1\text{--}5$) alloys used in this work was prepared by using vacuum induction melting method. Pure Mg and Y were placed in a magnesia crucible to melt and cast alloys. The whole melting and casting procedures were performed in a pure helium atmosphere to prevent oxidation. A proper excess of Mg over-composition (7 wt%) are necessary to compensate for the evaporative loss during smelting process. After the complete melting of raw Mg and Y ingots, the molten alloys were poured into an iron mold and cooled to room temperature. The prepared columnar ingots have a diameter of 30 mm and height of about 80 mm, as shown in Fig. 1. Then the alloy ingots were mechanically crushed into fine powders below 200 mesh for hydrogen storage performance tests. The photograph of pulverized powder sample is also exhibited in Fig. 1. For the sake of easy expression, the alloys with different Y quantity are designated as Y_1 , Y_2 , Y_3 , Y_4 and Y_5 alloy.

2.2. Structural characterization

The phase composition was performed by using a Bruker D8 Advance X-ray diffractometer (XRD) with $\text{Cu-K}\alpha$ radiation. Identification of the species was computer aided, using JCPDF files. Morphological studies of the alloy ingots were characterized by scanning electron microscopy (SEM, FEI Quanta-400). Before SEM tests, the alloy ingots were cut into small pieces. One of the cross section were polished by using different number (from small to big number) of grinding papers and later by using diamond abrasion pastes. Then the microstructures of the samples were directly observed by SEM without any corrosion. High resolution morphologies of the powder samples were carried out by transmission electron microscopy (TEM, FEI Tecnai G2 F20 S-TWIN). The TEM specimens were prepared by sonication of the powder samples (passed through a 300 mesh sifter) in ethanol and dipping of the suspension liquid on holey carbon film supported by a copper grid. The lattice spaces were directly measured according to the scale bar in TEM images by using Digital Micrograph software. In order to minimize the measurement errors, more than 20 adjacent atomic planes were included in each measurement. Every lattice space was measured for 5 times, and then calculated the average results and standard errors. The calculated lattice space values were indexed to the

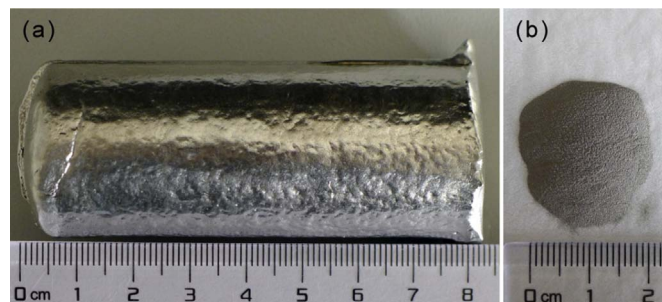


Fig. 1. Photographs of the selected Y_3 alloy: (a) alloy ingot prepared by vacuum induction melting; (b) pulverized powder sample (passed through a 200-mesh sifter).

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