Preparation and hydrogen storage properties of Mg-Al-Li solid solution

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ABSTRACT

In this work, a Mg-Al-Li solid solution was prepared and the influence of the preparation process on its hydrogen storage properties was investigated. The $Mg_{17}Al_{12}$ (Li) solid solution was obtained by sintering, annealing at liquid nitrogen temperature and mechanical ball milling using a molar ratio of Mg:Al:LiH = 6.5:1.5:2.0. The maximum hydrogen storage capacity of the $Mg_{17}Al_{12}$ (Li) solid solution reached 3.7 wt.% at 300 °C in 80 min. The enthalpy of the solid solution hydride decomposition was 53 kJ mol^{-1} H$_2$, much lower than that of bulk Mg hydride decomposition (75 kJ mol^{-1} H$_2$). The solid solution had higher hydrogen storage capacity and better hydrogen absorption kinetics than $Mg_{17}Al_{12}$ alloy.

Introduction

Mg, Al and Li are the most promising candidates for use as on-board hydrogen storage materials, having reversible hydrogen storage capacities of 7.76, 10.0 and 12.5 wt.%, respectively. Unfortunately, their practical application has been hindered by their poor reversible hydrogen absorption-desorption performance. For example, it is well known that the limitations for MgH$_2$ are thermodynamic stability (up to 350 °C for hydrogen release) and slow kinetics [1,2]. In contrast, AlH$_3$ decomposes into Al and H$_2$ at 170 °C, and the decomposition enthalpy is only 10 kJ mol^{-1} H$_2$ [3,4]. Although Mg and Al cannot be used as hydrogen storage materials directly, the thermodynamic properties of MgH$_2$ and AlH$_3$ are complementary. The integrated hydrogen storage performance of Mg-based hydrogen storage materials has been improved effectively by the addition of Al [5—9]. For example, by doping with Al, the dehydrogenation enthalpy of Mg$_{95}$Al$_5$ hydride is 72.1 kJ mol^{-1} H$_2$ [5], slightly lower than the bulk Mg hydride decomposition enthalpy of 75 kJ mol^{-1} H$_2$ [10]. The enthalpy of hydride formation for the Mg-Al system (62.7 kJ mol^{-1} H$_2$) was even lower than that for Mg$_2$Ni (64.5 kJ mol^{-1} H$_2$) [9].

Although Al is a key element to improve the thermodynamic properties for Mg-based hydrogen storage alloys, the overall performance of these types of alloy are not satisfactory for practical applications. Recently, modem nanotechnology has been introduced for preparation of Mg-based hydrogen

storage alloys [11–15]. It has been reported that a Mg-Co solid solution with body-centered cubic (BCC) structure was formed when a $Mg_{50}Co_{50}$ composite was milled for 100 h, and that this material could absorb hydrogen at 100 °C [11]. It is interesting that the BCC structure was unchanged during hydrogenation below 160 °C [12]. Furthermore, Sohn et al. [13] investigated a $10MgH_2/TiH_2$ system using a different preparation, and found that the temperature for the onset of dehydrogenation fell from 225 °C to 101 °C as the ball milling time increased from 30 min to 4 h. These results indicate that the hydrogen storage properties of Mg-based composites can be improved by using modern nanotechnology. In view of the high hydrogen storage capacities and complementary thermodynamic properties of Mg, Al and Li, a ternary Mg-Al-Li solid solution was prepared and the effect of the preparation process on hydrogen storage properties was investigated.

Experimental

Powders of Mg (purity > 99.5%, 300 mesh), Al (purity > 99.5%, 250 mesh) and LiH (>99.9 wt.%, 200 mesh), purchased from Alfa Aesar, were used as raw materials. The Mg, Al and LiH powders were mixed in a molar ratio of 6.5:1.5:2.0 and compressed into tablets under an applied pressure of 20 MPa for 5 min. The tablets were sintered at 450 °C for 4 h in a high vacuum resistance furnace and subsequently cooled with furnace temperature (designated as M-A-L-1) or quenched in liquid nitrogen (designated as M-A-L-2). The samples were mechanically milled under an argon atmosphere in a planetary mill (QM-WX04) with a ball to powder mass ratio of 40:1 at 400 rpm. The phase structure of the samples was characterized by X-ray diffraction (XRD) using a Rigaku-3015 X-ray diffractometer with Cu Kα radiation at 40 kV and 200 mA. The hydrogenation and dehydrogenation testing was carried out on an automatic Sieverts-type apparatus. Differential scanning calorimetry (DSC) of the samples was performed using a simultaneous thermal analyzer (Setaram Labsys Evo). All samples were well activated before testing.

Results and discussion

Phase structure

The XRD patterns of the Mg-Al-Li composite cooled with furnace temperature (M-A-L-1) and quenched in liquid nitrogen (M-A-L-2) are shown in Fig. 1. The two samples were mainly composed of $Mg_{17}Al_{12}$, $Mg_{0.42}Al_{0.58}$, Mg_2Al_3 and Li, suggesting that the two preparation processes had the same effect on the phase structure of the composite. The lattice parameters for the $Mg_{17}Al_{12}$ and Mg_2Al_3 phases, calculated from the XRD data using Jade 6.0 software, are listed in Table 1. As shown, the cell volume of the Mg_2Al_3 phase was almost the same for M-A-L-1 and M-A-L-2. The two annealing methods, cooling with furnace temperature and non-equilibrium quick quenching at liquid nitrogen temperature, had the same effect on the Mg_2Al_3 phase. However, the cell volume of the $Mg_{17}Al_{12}$ phase shrank when quick quenched at liquid nitrogen temperature. The cell volume of the $Mg_{17}Al_{12}$
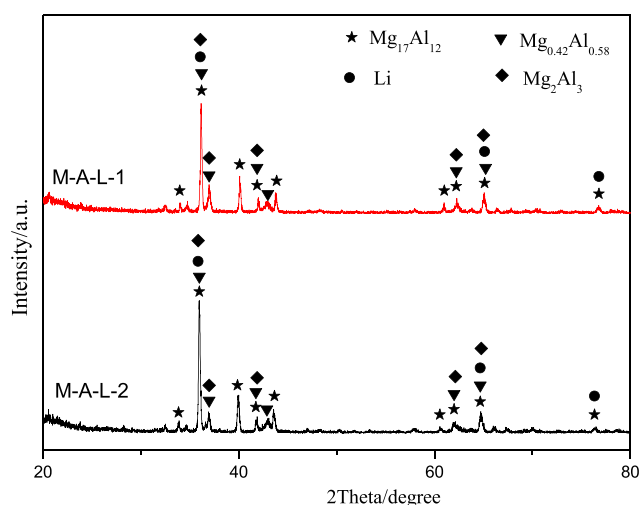

Fig. 1 – XRD patterns of the Mg-Al-Li composites.

phase was 1179.4 $Å^3$ when cooled with furnace temperature, which reduced to 1168.7 $Å^3$ when quenched at liquid nitrogen temperature.

Hydrogen storage properties

To understand the effect of the annealing method on hydrogen storage performance of the Mg-Al-Li composites, the hydrogen absorption/desorption kinetics of the composites were analyzed at 300 °C and are shown in Fig. 2. The two samples show the same hydrogen absorption kinetic performance and hydrogen storage capacity of approximately 2.9 wt.%. However, as shown in Fig. 2(b), the sample quenched at liquid nitrogen temperature showed better hydrogen desorption dynamic performance than that cooled with furnace temperature. The hydrogen release rate for M-A-L-2 was faster than for M-A-L-1 and released 2.85 wt.% hydrogen, equivalent to a hydrogen desorption efficiency of approximately 95.6%. The hydrogen released by M-A-L-1 was only 1.94 wt.%, equivalent to a hydrogen desorption efficiency of 68.3%. Quenching at liquid nitrogen temperature had a favorable impact on hydrogen desorption kinetics of the Mg-Al-Li composite.

Table 1 – The lattice parameters of the Mg-Al-Li composites.

Sample	Phase	Lattice parameters		Cell volume
		a = b (Å)	c (Å)	V (Å³)
M-A-L-1	$Mg_{17}Al_{12}$	10.57	10.57	1179.4
	Mg_2Al_3	5.80	9.58	279.4
M-A-L-2	$Mg_{17}Al_{12}$	10.53	10.53	1168.7
	Mg_2Al_3	5.79	9.64	279.5
M-A-L-2-35	$Mg_{17}Al_{12}$	10.58	10.58	1182.9
M-A-L-2-35: 1st dehydrogenation	$Mg_{17}Al_{12}$	10.59	10.59	1186.2
M-A-L-2-35: 3rd dehydrogenation	$Mg_{17}Al_{12}$	10.59	10.59	1186.2