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Phase transition and hydrogen storage properties of $Mg_{17}Ba_2$ compound

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ABSTRACT

$Mg_{17}Ba_2$ hydrogen storage alloy was obtained by induction melting, and its hydrogen storage properties and phase transitions have been investigated. The reversible hydrogen capacity of $Mg_{17}Ba_2$ compound was 4.0 wt% H_2. A three-step dehydrogenation mechanism was revealed for the first time, and a new hydride ($Ba_2Mg_7H_{18}$) was discovered during the dehydrogenation process. Enthalpy and entropy changes for the dehydrogenation of $Mg_{17}Ba_2$ were also calculated.

1. Introduction

Magnesium (Mg)-based hydrogen storage alloys are considered to be one of the most promising hydrogen storage alloys because of their high hydrogen capacity (e.g., 7.6 wt% H_2 for MgH_2), abundant resources, and environmental friendliness [1]. However, their relatively high thermal stability and sluggish kinetics limit their on-board applications [2,3]. To solve these obstacles, various methods have been explored, such as alloying [4,5], changing the reaction pathway [6–8], nanostructuring [9,10], and doping with catalysts [11,12], etc. Among these methods, alloying or changing the reaction pathway is an effective way to improve thermodynamic and/or kinetic properties.

On one side, alloying Mg with a low melting point metal may lead to a high atomic diffusion rate in the alloy and accelerate the de/hydrogenation kinetics [13]. On the other side, Alloying elements (e.g., Si, Al, Ge), which may react with Mg and form more stable compounds, could change the reaction pathway and lower the dehydrogenation enthalpy. Vajo et al. [14] found that alloying Mg with Si can reduce the enthalpy significantly. They further revealed that the pathway of the dehydrogenation reaction had been changed. Zlotea et al. [15] suggested that Mg-rich intermetallic compounds $Mg_{24}Y_5$ react with hydrogen to yield one-dimensional MgH_2 nano-structures through a disproportionated reaction. Recently, Bhihi et al. [16] using ab initio calculations, predicted that alloying MgH_2 with small amounts of alkaline metals (Sr, Ba) can destabilize MgH_2 significantly. There are many intermetallic compounds in the Mg-Ba system (e.g., $Mg_{17}Ba_2$, $Mg_{23}Ba_6$, Mg_2Ba) [17], however, there are few study about the hydrogen storage properties of Mg-Ba system. To obtain alloys with high hydrogen capacity, Mg-rich intermetallic $Mg_{17}Ba_2$ compound were investigated.

This paper reported the hydrogen storage properties and phase transition of $Mg_{17}Ba_2$ compound for the first time during hydrogenation/dehydrogenation and hydrogen storage properties of $Mg_{17}Ba_2$. The enthalpy (ΔH) and entropy (ΔS) for the hydrogenation/dehydrogenation reaction were also measure. A new hydride, $Ba_2Mg_7H_{18}$ was discovered and a reversible hydrogen storage capacity of 4.0 wt% H_2 of $Mg_{17}Ba_2$ compound was obtained.

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2. Experimental

$Mg_{17}Ba_2$ was obtained by induction melting under the protection of pure argon atmosphere. Firstly, bulk Mg (99.5%, Alfa Aesar) and Ba (99.9%, Alfa Aesar) were weight out in mole ratio of 17:2, and 5 wt%. Mg more than the mole ratio was added to compensate its evaporation loss during melting. The compound was heated up to ~1073 K for 15 min. After removing the oxidation layer, ingots were pulverized and screened through a 200 mesh sieve. All handling, was performed in a glove box equipped with a recirculation and regeneration system, which maintained the oxygen and water concentrations below 5 ppm and 1 ppm, respectively.

The phase structure of all samples was characterized using a Philip X'Pert Pro X-ray diffraction (XRD) instrument with CuK_α radiation ($\lambda = 1.5406$ Å). During testing, samples were covered with liquid paraffin wax or transparent protective film (3M Company) to prevent oxidation. Synchrotron powder X-ray diffraction data were collected using a Mythen-II detector at a wavelength of 0.5893 Å at the Powder diffraction beamline, Australian Synchrotron. Before testing, the fine powder sample was loaded into a pre-dried 0.7 mm boron-silica glass capillary inside an argon-filled glovebox. The capillary was sealed with vacuum grease for PXRD measurements. Sample was kept under 1 atm of high purity Ar atmosphere (99.999%).

The hydrogenation/dehydrogenation behavior was measured by pressure-composition-isotherm (PCI) at different temperatures using a commercial Sieverts-type apparatus (Gas Reaction Controller, Advanced Materials Corporation). The measuring temperature of the sample was controlled using a furnace with ±2 K accuracy. Prior to hydrogenation, samples were subjected to three activation cycles. The activation processes were set as follows: the sample holder was heated up to 653 K and vacuumed for 30 min, and then 8 MPa hydrogen gas was allowed to react with the samples for 30 min. To calculate ΔH and ΔS, the H pressure at the midpoint of the desorption pressure platforms of the measured PCI curves was taken as the data of the platform pressure in the van't Hoff plot.

3. Results and discussion

Fig. 1 shows the XRD patterns of as-cast, hydrogenated and dehydrogenated $Mg_{17}Ba_2$ compounds. As shown in Fig. 1(a), the as-cast sample was indexed as $Mg_{17}Ba_2$. And then the sample was executed to hydrogenation for 2 h at 653 K under 8 MPa H_2, which XRD patterns were shown in Fig. 1(b). Interestingly, except for some diffraction peaks of MgH_2, the remaining peaks cannot be identified as any phase in the Mg-Ba-H system. Thus, we assume that a new unknown phase (X phase) may exist, and its detailed information will be discussed later. The results above indicated that $Mg_{17}Ba_2$ may react with hydrogen to form MgH_2 and the X phase during hydrogenation. Fig. 1(c) shows the XRD patterns of the dehydrogenated sample. After dehydrogenation, the MgH_2 and X phases disappeared, while Ba_2MgH_6 and Mg phases formed together with a small amount of $Mg_{17}Ba_2$ phase.

To obtain the thermodynamic parameters and hydrogen storage properties of $Mg_{17}Ba_2$, three hydrogenation/dehydrogenation cycles of PCI experiments were carried out at 613, 633, and 653 K, and the results were presented in Fig. 2. As shown in Fig. 2(a), $Mg_{17}Ba_2$ compound could absorb 4.3 wt% H_2 and release 4.0 wt% H_2. Thus, its reversible hydrogen storage capacity is 4.0 wt% H_2. The PCI curve at 613 K was fluctuant, mainly because of the poor sample kinetic properties and the limited measurement interval.

As shown in Fig. 2(a), there is only one hydrogenation platform in all PCI curves, but there are three dehydrogenation platforms in the PCI curves at 633 and 653 K. According to the desorption pressure, these three dehydrogenation platforms are named as high, medium, and low platforms. The reversible hydrogen storage capacities of high, medium, and low platforms were 2.3, 1.4, and 0.3 wt% H_2, respectively. However, because of the limitation of the apparatus, low platforms was too low to be detected in the PCI

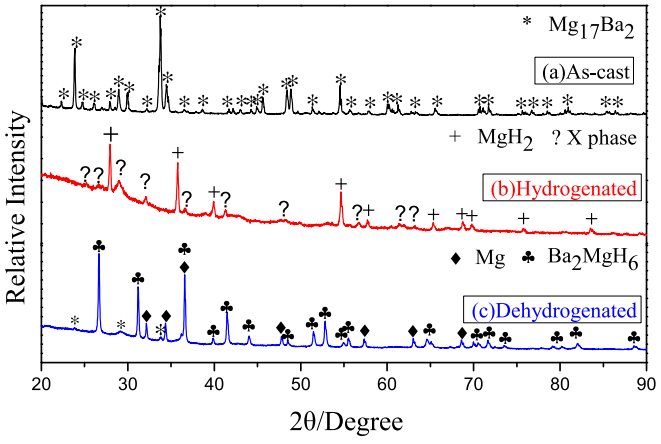

Fig. 1. XRD patterns of (a) as-cast, (b) hydrogenated, and (c) dehydrogenated $Mg_{17}Ba_2$ compounds.

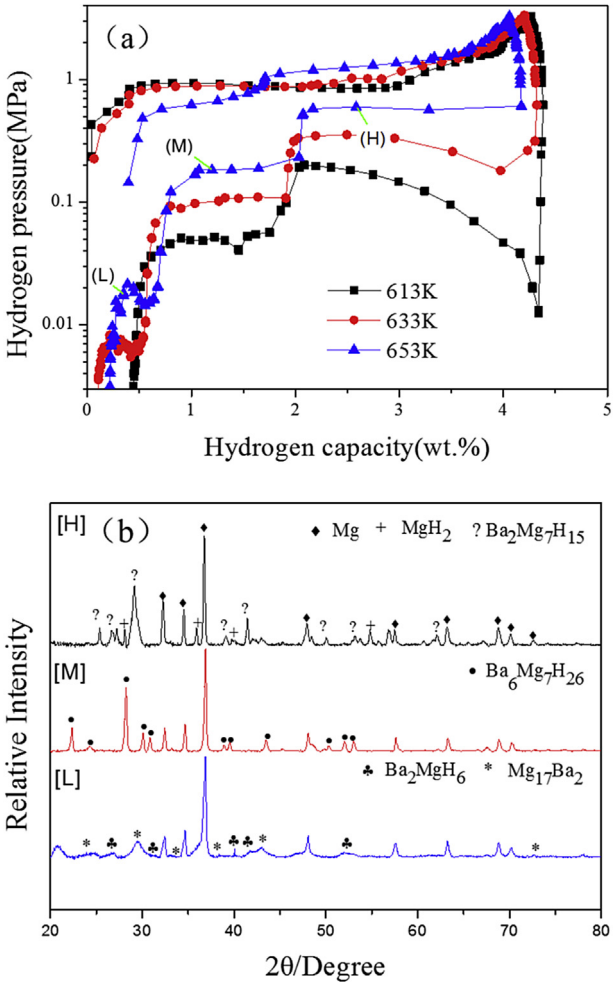

Fig. 2. (a) PCI curves of $Mg_{17}Ba_2$ compound measured at different temperatures and (b) XRD profiles of points (H), (M), and (L) in the PCI curves.