



## Short communication

Significantly improved hydrogen desorption property of La<sub>2</sub>Mg<sub>17</sub> alloy modified with Ni–Al nanocrystalline

Huaiwei Zhang, Xinyao Zheng, Teng Wang, Xingguo Li\*

College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

## ARTICLE INFO

## Article history:

Received 2 November 2015

Received in revised form

26 November 2015

Accepted 28 November 2015

Available online 14 December 2015

## Keywords:

Hydrogen storage alloys

Nanocrystalline catalyst

PVD method

Rare earth metals

## ABSTRACT

A simple method was developed for improving the hydrogen storage properties through adding nano Ni–Al compounds using as a stable catalyst to the La<sub>2</sub>Mg<sub>17</sub> alloys by a PVD method. With the trace addition of the catalyst, hydrogen absorption and desorption rate are all substantially improved for the La–Mg based alloys. The alloys formation process has been determined, and the activity energy of the hydride dehydrogenation reaction before and after Ni–Al nanocrystalline addition was also calculated.

© 2015 Elsevier Ltd. All rights reserved.

In recent years, hydrogen as an alternative to conventional fuels plays a very important role in the modern society. As we know, the intermetallic compounds for hydrogen storage materials are generally made up of hydrogen absorbing elements (A) and non-hydrogen-absorbing elements (B). But another type of compounds with magnesium-rare-earth-metal (RE) composition attract us more and more considerable interests as hydrogen storage materials for the higher hydrogen storage capacity [1–6].

For the compounds of magnesium with rare earth metals, various methods has been used for synthesizing the hydrogen storage alloys and improving the hydrogen storage properties, such as reactive ball milling (RBM) [4,7] rapid solidification (RS) [8–11] and equal channel angular pressing (ECAP) [12], and so on. But there were few related reports for the application of trace doping modification method to the hydrogen storage alloys. Ouyang et al. [3] prepared the Mg<sub>3</sub>LaNi<sub>0.1</sub> alloy with more rapid hydriding/dehydriding kinetics than Mg<sub>3</sub>La by induction melting. Li et al. [13] studied the effects of nano Mo–Ni compound additives to the La–Mg–Ni-based hydrogen storage alloys. They considered that the Mo–Ni compound showed a high electro-catalytic activity, and worked as a catalyst to charge the transfer reaction at the alloy surface. Li et al. [14] thought that the crystal structure could transfer to amorphous one with the increasing amount of Ni

powders in the La<sub>2</sub>Mg<sub>17</sub> alloy through ball milling method. Liu et al. [15] investigated that the addition of LiBr in La<sub>2</sub>Mg<sub>17</sub> alloys directly affects the dynamic performance of composite materials produced by ball milling.

The present paper reports, for the first time, a new hydrogen storage alloy of Ni–Al@La<sub>2</sub>Mg<sub>17</sub> and its properties. For this material, the Ni–Al alloy was presented mainly as nanocrystalline, and well dispersed in the body alloy. NiAl alloy with higher binding energy are often used as the high-temperature compounds. Under the micro scale, there was no reaction occurred with other elements in the La–Mg–Ni–Al phase diagram. NiAl nanocrystalline could be thus stably existed in the system. In this research, the trace high temperature and stability materials which were consider as a catalyst dispersion additive in hydrogen storage alloys was also first investigated.

The body alloy of La<sub>2</sub>Mg<sub>17</sub> ingots were prepared by induction melting of high-purity Mg (Beijing, 99.9%) and La (Beijing, 99.9%) in a graphite crucible under pure helium atmosphere. In order to avoid the evaporation of Mg element during the melting process, the temperature was maintained at between 923 K and 973 K. The as-cast samples was followed by an annealing step under 773 K for 24 h. The alloys were pulverized by ball milling under an argon atmosphere for 2 h with 200 rpm, and the particle size was about (50–70) μm. Magnetron sputtering system under high pure Argon was adopted as the PVD (Physical Vapor Deposition) doping method. We could control the Ni and Al adding content with about 2 wt. % by adjusting the sputtering time and power. Ni–Al

\* Corresponding author.

E-mail address: [xgli@pku.edu.cn](mailto:xgli@pku.edu.cn) (X. Li).

compounds were formed followed by an annealing step.

The alloys were characterized by a scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDXS), X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM). The hydrogen storage properties of the alloys were measured using Sieverts method on testing apparatus (made by Hy-Energy in USA). DSC measurements were performed using DSC 204 HP Phoenix made by Netzsch. The set of samples consisted of about 10 mg contained in an aluminum crucible and subjected to different heating rates of 2, 5, 10, 15 and 20 K/min from room temperature to about 773 K under a flow rate of argon at 100 ml/min at 0.1 MPa. The DSC measurement was contacted with a mass spectrum analyzer (MS), and the delaying time is 5 s.

The XRD patterns of the as-melted  $\text{La}_2\text{Mg}_{17}$  and  $\text{Ni-Al@La}_2\text{Mg}_{17}$  alloy at the scanning speed of  $0.5^\circ/\text{min}$  were shown in Fig. 1a. As shown in Fig. 1(a), there were about 19 diffraction peaks which can be excellently indexed with space group  $P63/mmc$  for the  $\text{La}_2\text{Mg}_{17}$  sample. For the  $\text{Ni-Al@La}_2\text{Mg}_{17}$  alloy, a new NiAl peak appeared at the 2-theta value of about  $25^\circ$ . But the lattice constant of the  $\text{La}_2\text{Mg}_{17}$  phases were unchanged for these two samples, it indicated that the trace amount of NiAl addition have not cause the macro-phase change of the body intermetallic alloys. The EDS images were demonstrated in Fig. 1b for the  $\text{Ni-Al@La}_2\text{Mg}_{17}$  alloys. The picture showed that the Aluminum and Nickel element were accompanied in the sample. This result further illustrated that the nanocrystalline NiAl alloys did not react with the body phase in this process. The formation of the  $\text{Ni-Al@La}_2\text{Mg}_{17}$  alloy used PVD method could simply summarize as Fig. 1c, and tested by the TEM analysis. The TEM images revealed that the electron diffraction patterns with a bigger radius of the final product  $\text{Ni-Al@La}_2\text{Mg}_{17}$

was probably belonged to NiAl phase with lattice distance of about 0.0091 nm in (2 0 7) crystallographic plane.

Introduction of NiAl into the body alloys to reach a composition  $\text{Ni-Al@La}_2\text{Mg}_{17}$  had positive effects on the hydrogenation kinetics. The hydrogen absorption/desorption behaviors of the alloys for the first hydrogenation cycle at 573 K with initial hydrogen pressure of 2 MPa and hydrogen desorption pressure of 0.02 MPa was demonstrated in Fig. 2a, and a huge difference in the kinetics of both hydrogenation and dehydrogenation can be seen.

The PCI curves were also measured at 573 K about the  $\text{La}_2\text{Mg}_{17}$  and  $\text{Ni-Al@La}_2\text{Mg}_{17}$  alloys, in Fig. 2b. As seen from the PCI curves, the reversible hydrogen storage of the two alloys is close and about 3.5 wt.% (hydrogen capacity of pressure plateau region). But the results showed that  $\text{Ni-Al@La}_2\text{Mg}_{17}$  alloy was superior to the pure  $\text{La}_2\text{Mg}_{17}$  alloy in plateau slope and plateau pressure hysteresis between absorption and desorption process. This reveals that the hydrogen storage properties of  $\text{La}_2\text{Mg}_{17}$  alloys with nanocrystalline are more stable during the hydrogenation and dehydrogenation process. The hydrogen absorption/desorption cycle curves which were displayed in Fig. 2c also proved this viewpoint. The system maintained above 95% of its maximum hydrogen storage capacity after 10 cycles.

Fig. 3 shows the DSC curves of alloys tested at heating process. For pure  $\text{La}_2\text{Mg}_{17}$  alloy, only one peak with the temperature of about 700 K was observed at the DSC heating trace. But there were two peaks at the temperatures of about 600 K and 720 K in the heating process for  $\text{Ni-Al@La}_2\text{Mg}_{17}$  alloys. Due to the higher decomposition temperature [16], these three peaks all corresponded to the hydrogen desorption points with a single Mass Spectrum (MS) test. The different DSC phenomenon for two alloys

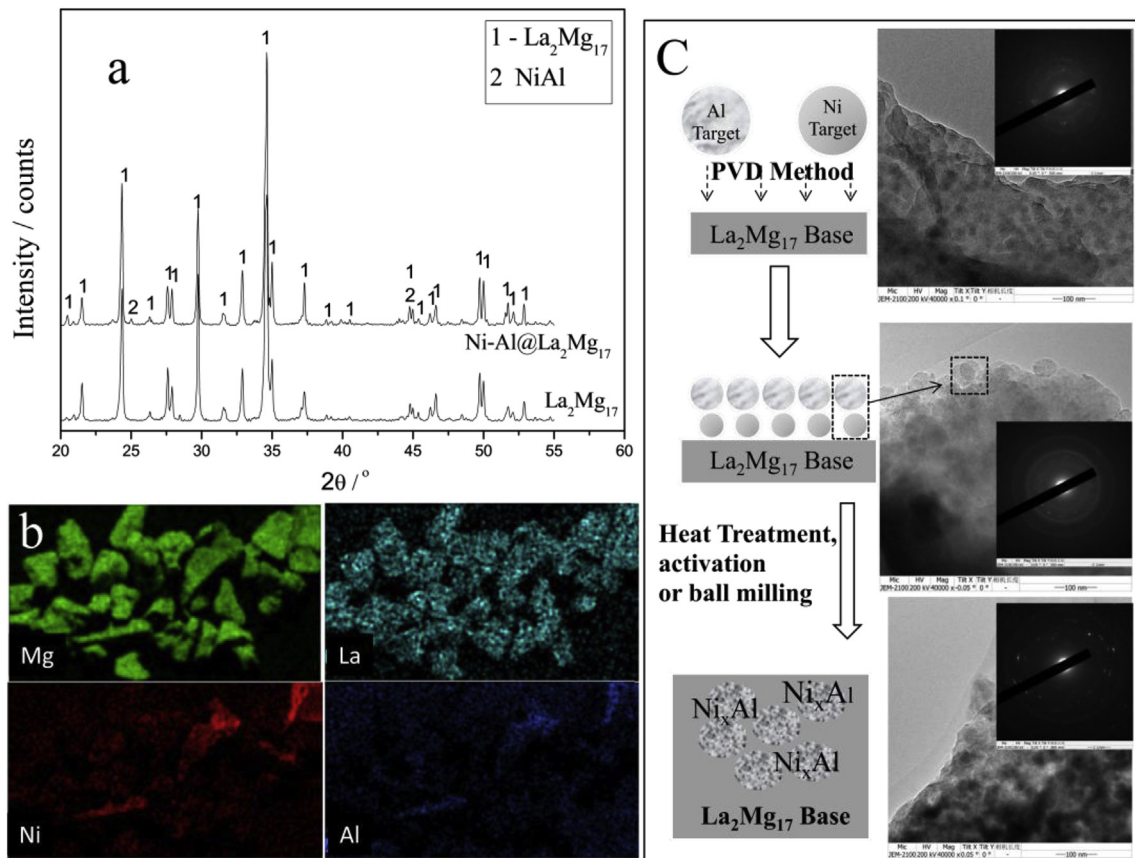


Fig. 1. The formation process and phase structure of  $\text{Ni-Al@La}_2\text{Mg}_{17}$  Alloys.

Download English Version:

<https://daneshyari.com/en/article/1599676>

Download Persian Version:

<https://daneshyari.com/article/1599676>

[Daneshyari.com](https://daneshyari.com)