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Ni-Al films induced surface modification of La_2Mg_{17} alloy leading to improved dehydrogenation properties

Huaiwei Zhang[a,*], Li Fu[a], Weidong Xuan[b,**], Haiying Qin[a], Zhenguo Ji[a]

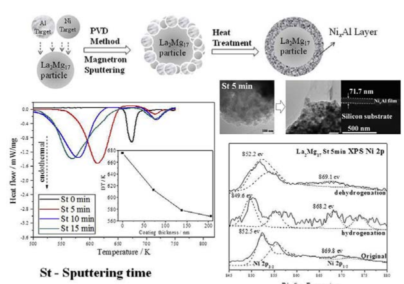
[a] *College of Materials and Environmental Engineering, Hangzhou Dianzi University, Hangzhou 310018, PR China*

[b] *State Key Laboratory of Advanced Special Steel, Shanghai Key Laboratory of Advanced Ferrometallurgy, School of Materials Science and Engineering, Shanghai University, Shanghai 200072, PR China*

HIGHLIGHTS

- Ni-Al nano-film coatings are applied to the La_2Mg_{17} alloy modification.
- The reversible hydrogen storage properties are improved significantly.
- Ni-Al nanocrystalline as the catalyst is confirmed after 20 cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

The effects of surface coating with Ni-Al nano-films to the hydrogenation properties of the La_2Mg_{17} alloy are studied in the paper. The reversible hydrogen storage capacities, thermodynamics and kinetics process are all improved for the coating samples, and the comprehensive performances reach the best when the sputtering time is 5min with the film thickness 71.7 nm. The dehydrogenation temperature of the coating sample can be reduced to about 560K from above 720K comparing to the body alloy. The XPS analysis shows that the Ni-Al film coating layer can act as the catalyst in the dehydrogenation process.

1. Introduction

Some of La-containing Mg-riched intermetallic compounds have been concerned for the hydrogen storage alloys, such as La_2Mg_{17} and $LaMg_{12}$. But the higher thermal dehydrogenation temperature and the lower reaction activity are the main limited factors for their further application [1–6]. The hydrogen absorption/desorption process is greatly affected by the surface conditions of the materials. For the past few years, surface coating or modification as the effective method to improve the materials performances have attracted more and more attentions [6–10].

The Mg-based hydrogen storage alloy modified with various compounds showed great advantage in the hydrogen absorption and desorption process [11–15]. Ouyang et al. [16–18] investigated that the comprehensive performances of Mg-based hydrogen storage alloys could be improved significantly after trace metal elements doping process. The obtained results point to a method for improving not only the thermodynamic but also the kinetic properties of hydrogen storage materials, and these papers also draw a new idea of dual-tuning effects [19,20]. The electrochemical performances of Mg_2NiH_4 can be effectively improved through surface modification with nano-nickel because of the excellent catalytic activity and outstanding electrical

* Corresponding author.
** Corresponding author.
E-mail addresses: zhw5984@hdu.edu.cn (H. Zhang), wdxuan@shu.edu.cn (W. Xuan).

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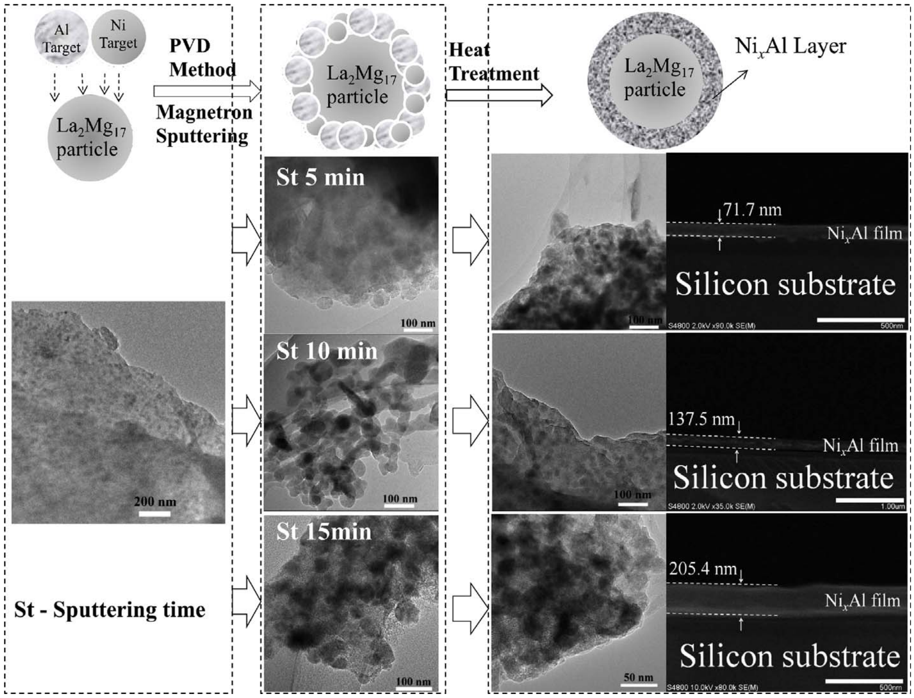

Fig. 1. The formation process and phase structure of Ni-Al@La_2Mg_{17} coatings.

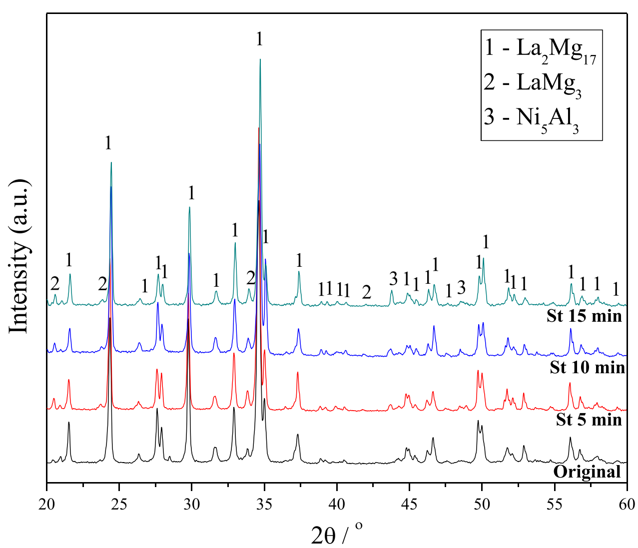

Fig. 2. XRD analyses of Ni-Al@La_2Mg_{17} alloys with various *St*.

conductivity [21].

Hou et al. [22] investigated the La-doped Mg_2Ni alloys, and the improvement of phase microstructures can improve the electrode catalytic activity and hydrogen diffusivity. Li et al. [23] studied the surface coating of $Nd_{0.7}Mg_{0.3}Ni_3$ alloy with Ni and Co via an electroless plating method, and the improvement of the properties is contributed to the higher catalytic activity and the protective function of the coating layers. Reduced graphene oxide was also been successfully coated on the Mg_2Ni alloy via electrostatic assembly, and the anti-corrosion and electrochemical properties for the alloy were improved greatly [24,25]. In our previous studies, the electrochemical performances of La-Mg based alloys were also enhanced with changing the surface conditions by magnetron sputtering methods [26].

In order to promote the hydrogen storage properties of the La-Mg based alloys, nano-scale Ni-Al layer was prepared on the surface by the PVD (Physical Vapor Deposition) coating method. The effects of the metallic layer on dehydrogenation performances of the alloys are subsequently investigated. The structure transition relevant to the properties of the alloys is also discussed.

2. Experimental and methods

The as-cast alloy of La_2Mg_{17} was prepared by induction melting method with high-purity magnesium and lanthanum metals under pure helium atmosphere, and the alloys was annealed under 973K (700 °C) for 7 days. The alloys were pulverized to about (50–70) μm through ball milling process under an argon atmosphere. Magnetron sputtering system under high pure Argon was adopted as the PVD coating method. We could control the Ni-Al film thickness by adjusting the sputtering time (St).

Some silicon substrates were coated at the same time, and the accurate thickness of the films could be obtained to examine their cross section thickness through the scanning electron microscopy with an energy-dispersive X-ray spectroscopy (SEM-EDXS, Hitachi S4800, 10 kV). The alloys were characterized by X-ray diffraction (XRD, Rigaku D/max 2000 diffractometer, Cu Kα), transmission electron microscopy (TEM, JEOL JEM-2100, 200 kV), X-ray photoelectron spectroscopy (XPS, AXIS-Ultra, Kratos Analytical, Al Kα) and differential scanning calorimeter (DSC, NETZSCH DSC 204 HP Phoenix). The hydrogen storage properties of the alloys were measured using Sieverts method with initial hydrogen pressure of 2 MPa and hydrogen desorption pressure of 0.1 MPa.

3. Results and discussion

3.1. Formation process and structures

The process of the La_2Mg_{17} alloy with Ni-Al coating (Ni-Al@ La_2Mg_{17}) used PVD method can simply summarize as Fig. 1. There are three steps for the surface film formation: magnetron sputtering to the alloy particles, particle surface absorption and heat treatment molding. The TEM image can obviously illustrate the gradual process of change during the various steps. The coating thickness is 71.7 nm, 137.5 nm and 205.4 nm (for St 5min, 10min and 15min), respectively.