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Structure, hydrogen storage kinetics and thermodynamics of Mg-base Sm_5Mg_{41} alloy

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ABSTRACT

The composition, phase components, and microstructure of Mg-based Sm_5Mg_{41} alloy prepared by vacuum induction melting technique were investigated by X-ray diffraction (XRD), scanning electron microscope (SEM) and high resolution transmission electron microscopy (HRTEM). The gaseous hydrogen ab/desorption properties of the alloy were measured by an automatically controlled Sieverts apparatus. The results indicate that the as-cast alloy consists of two phases, major phase Sm_5Mg_{41} and secondary phase $SmMg_3$. The MgH_2 and Sm_3H_7 phases form after hydrogen absorption, while Mg and Sm_3H_7 phases exist after hydrogen desorption at 340 °C. Field Emission Transmission Electron Microscopy (FETEM) observation reveals the microstructure and phase distribution of Mg-based Sm_5Mg_{41} alloy before and after hydrogen absorption and the hydriding and dehydriding reaction pathways as follow: $Sm_5Mg_{41} + SmMg_3 + H_2 \rightarrow Sm_3H_7 + MgH_2 \leftrightarrow Sm_3H_7 + Mg + H_2$. The hydrogen storage thermodynamics and kinetics of the Mg-based Sm_5Mg_{41} alloy are improved as a result of the formation of the Sm_3H_7 nanoparticles. Consequently, the starting dehydrogenation temperature of the alloy hydride is about 270 °C. The dehydrogenation and hydrogenation activation energies of the alloy are estimated to be 135.28 and 77.802 kJ/mol, which suggests that the Sm_3H_7 nanoparticles play a beneficial role to reduce the total potential barrier that the hydrogen absorption or desorption reaction must overcome. The hydrogenation enthalpy of the alloy was determined to be −76.52 kJ/mol H_2, indicating that adding Sm can slightly alter the hydrogen absorption thermodynamic property of Mg-based alloy. The desorption property improved by alloying Sm is attribute to the enhanced kinetics rather than the variation in the thermodynamics.

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Introduction

Generally, traditional car exhaust fumes containing toxic gas mixture, including carbon dioxide, carbon monoxide, hydrocarbons, benzene and suspended particles. Encouragingly, Mirai hydrogen fuel cell vehicle newly developed by Toyota exhausts only water and no pollution, and its speed can be up to 178 km/h. Fuel cell car is driven by electricity produced from the chemistry of hydrogen and oxygen, and also belongs to a kind of electric vehicle (EV) which just add a fuel cell and a hydrogen gas [1]. Essentially, fuel-cell vehicle is regarded as the end solution of transportation due to the fact that it has not only the advantages of ordinary pure electric vehicles, but the endless source of hydrogen and oxygen, and the convenient addition of hydrogen like refueling, without any pollution [2]. A key technical obstacle for the realization of onboard fuel-cell or hydrogen fueled vehicles is to develop a practical hydrogen storage system [1–3]. Among hydrogen storage methods, hydrogen storage in metal hydrides is considered to be one of the most promising alternatives to meet the requirements for mobile application [4]. Mg-based hydrogen storage alloys have shown promise in the fuel cell due to their high hydrogen content, easy accessibility and low cost, and possessing good quality functional properties, such as heat resistance, reversibility and recyclability [5,6]. However, the relatively high desorption temperature and sluggish releasing kinetics of their hydrides are the serious constraints to practical application [7]. Therefore, further improving the hydrogen storage performance of Mg-based alloys is still a major challenge faced by researchers in this area.

In the past decades, many efforts have been devoted to Mg-based materials to decrease their desorption temperature and improve the kinetics and cycle lifetime, such as alloying, preparation technology, appropriate catalyst, etc. [8,9] In these processes, different kinds of additives, including elements [10–12], compounds [13–16], and hydrogen storage alloys [17,18] are incorporated into the Mg matrix, resulting in a remarkable improvement of the hydrogen storage properties. La_2Mg_{17}, with a storage content of about 6 wt.%, absorbs hydrogen at about 350 °C [19]. The minimum desorption temperature of novel Mg-In-Ni ternary alloy reduced down to 230 °C [20]. Mg_3La compounds fabricated by induction melting can reversibly absorb/desorb 2.89 wt.% hydrogen at about 296 °C [21]. MgH_2 + 10 wt.% ZrNi composite could absorbed about 5 wt.% in less then 3 min and desorb the same amount in 7 min at 300 °C [22]. Mg_3Ag reversible system offered a method for adjusting the thermodynamic properties of Mg-based alloys [23]. Ouyang et al. [24] offer a novel technique, plasma milling, to dual-tune the kinetic and thermodynamic properties of Mg-based alloys. The dehydrogenation enthalpy change and activation energy of $Mg_{85}In_5Al_5Ti_5$ alloy synthesized by plasma milling decreased from 75 to 65.2 kJ/(mol H_2) and decreased to125.2 kJ/mol from the initial value of 160 kJ/mol, respectively [25]. Although many new results have been reported, further efforts are necessary to improve the hydrogen storage properties of Mg-based alloys.

It is also known that the alloying of Mg with RE elements (such as Y, Nd, Sm, Pr, Ce or La-rich mischmetal) can improve the hydrogen absorption and desorption rates [26–28]. Especially, Microstructural optimization of $REMg_{12}$, RE_2Mg_{17} and RE_5Mg_{41} alloys could be used as high performance hydrogen storage materials [29,30]. Amount of Sm resources are wasted by discharging waste water in many rare earth production enterprises because Sm lack of application areas and market requirements [31]. To apply Sm and decrease the desorption temperature and improve the kinetics of Mg-based hydrogen storage materials, the Mg-based binary alloy Sm_5Mg_{41} was fabricated by vacuum induction melting. The microstructures and gaseous storage hydrogen behaviors of the alloy were investigated in detail.

Experimental

The experimental alloys with a chemical composition of Sm_5Mg_{41} were prepared by using a vacuum induction furnace in a helium atmosphere under a pressure of 0.04 MPa. The mechanically ground alloy powders (particle size $\leq$ 75 μm) were prepared for measurement by manual grinding in an argon atmosphere to prevent the powders from being oxidized during crushing. Pressure-composition isotherms (P-C-I) and hydrogen absorption/desorption kinetics were measured by a Sieverts-type apparatus with a furnace controlled to an accuracy of ±1 °C. Prior to P-C-I measuring, 6 times hydrogen absorption and desorption cycles were performed at 340 °C to activate the 500 mg sample, which was loaded into a cylindrical reactor for each measurement. The P-C-I measured at 320, 340, 360 and 380 °C in a hydrogen pressure range from 0.05 MPa to 3 MPa. The hydrogen absorption was conducted at a pressure of 3 MPa and at 270, 300, 360, and 380 °C respectively, the hydrogen desorption at a pressure of 1×10^{-4} MPa and at 300, 320, 340, and 360 °C. The hydrogen desorption properties of the samples was evaluated with a thermal gravity analysis (TGA, Q600), and the analysis was performed with the experimental parameters of 5 °C/min heating rate and 35.1 mL/min high-purity argon (99.999%) flow rate. The phase compositions and structures of the materials were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM, Philips QUANTA 400), Field Emission Transmission Electron Microscopy (FETEM, Tecnai G2 F30) and high resolution transmission electron microscopy (HRTEM, JEM-2100F, operated at 200 kV) and their crystalline states were evaluated by selected area electron diffraction (SAED).

Results and discussion

Phase and microstructure changed by hydriding/dehydriding reaction

The Rietveld refinement of the observed XRD patterns of the as-cast and hydrogen absorption/desorption samples for Mg-based Sm_5Mg_{41} alloy are shown in Fig. 1. It can be seen that the as-cast alloy is composed of major phase Sm_5Mg_{41} (93.367 wt.%) with space group of *I*4*m* tetragonal structure ($a = b = 1.4815$ nm, $c = 1.0366$ nm) and 6.633 wt.% of secondary phase $SmMg_3$ with space group of *Fm*3*m* cubic structure (a = 0.7346 nm). The MgH_2 (56.298 wt.%) and Sm_3H_7 (43.702 wt.%) phases form after hydrogen absorption, while