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A TEM based study of the microstructure during room temperature and low temperature hydrogen storage cycling in MgH_2 promoted by Nb–V

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Abstract

Magnesium hydride combined with a new bimetallic Nb–V catalyst displays remarkably rapid and stable low temperature (200 °C) hydrogen storage kinetics, even after 500 full volumetric absorption/desorption cycles. The system is also able to fairly rapidly absorb hydrogen at room temperature at a pressure of 1 bar. This unprecedented absorption behavior was demonstrated for 20 cycles. We employed extensive cryo-stage transmission electron microscopy (TEM) analysis on fully and partially sorbed materials to provide insight into the rapid Mg to MgH_2 phase transformation. After extended cycling of what was initially a 1.5 μm thick fully dense alloy film, the sample structure becomes analogous to that of a weakly agglomerated nanocomposite powder. The cycled Mg–V–Nb structure consists of a dense distribution of catalytic Nb–V nanocrystallites covering the surfaces of larger Mg and MgH_2 particles. The partially absorbed 20 °C and 200 °C microstructures both show this morphology. TEM results combined with Johnson–Mehl–Avrami-type kinetic analysis point to the surface catalyst distribution and stability against coarsening as being a key influence on the two-stage hydriding kinetics. Remarkably, the mean size of the $Nb_{0.5}V_{0.5}H$ nanocrystallites stays essentially invariant throughout cycling; it is 3 nm after 45 cycles and 4 nm after 500 cycles. A mechanistic description is provided for the cycling-induced microstructural evolution in the ternary alloy as well as in the binary baselines.

Keywords: Hydrogen storage; Magnesium hydride; TEM; Microstructure; Catalyst

1. Introduction

Magnesium hydride (MgH_2) based systems are considered promising for solid-state hydrogen storage [1–4]. However, practical applications are hindered by the systems' excessive thermodynamic stability and sluggish hydriding/dehydriding kinetics [5,6]. The origins of the slow kinetics have been investigated using a variety of analytical techniques, such as in situ synchrotron X-ray diffraction [7], in situ or cryo-stage electron microcopy [8–10], first principles calculations [11], and neutron scattering [12–14]. There have been some recent promising studies where researchers have shown thermodynamic destabilization of MgH_2 through selective alloying [15–17] or creation of constrained nanolayered structures [18,19]. Some researchers have demonstrated that the sorption kinetics are significantly accelerated by intimately mixing or alloying proper transition metals with Mg [20–25]. A number of authors have also accelerated the kinetics by synthesizing nanoscale structures so as to reduce diffusion limitations [26–31], or by creating highly deformed structures with high dislocation densities [32–34].

Mg-based alloys, in thin film form, are currently subject to intense scientific inquiry. As a high-throughput screening method, thin film techniques are useful to identify the ideal compositions and amounts of secondary catalytic or

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destabilizing additives [35–37]. For example, by physical vapor depositing Mg films with suitable elements, such as Fe, Ti, V or Cr, it is possible to create materials with rapid sorption kinetics [38–40]. It is known that if the selected elements do not form intermetallic compounds with Mg or have appreciable solubility in Mg at equilibrium, they will segregate from the as-deposited supersaturated solid solutions of Mg and form separate phases [41]. The superb kinetic enhancement of such composite materials has been attributed to the catalytic effect of the secondary phases that are densely dispersed in the Mg matrix. Though the exact role of the secondary phase is yet to be determined, it has been hypothesized that it could serve as hydrogen dissociation/recombination catalysts, heterogeneous nucleation sites and high H diffusivity paths. The secondary phase may also act as pinning points forming a network along the Mg(MgH_2) grain boundaries [41]. This would prevent the growth of Mg grains and the sintering of Mg particles, reducing the diffusion distances. More work is needed in terms of providing direct microstructural evidence to demonstrate these arguments. For example, one unknown regards the systems' microstructural evolution during extended elevated temperature hydriding/dehydriding cycling and its relationship to the universally observed degradation of the kinetics. Another question concerns the microstructural origin of fundamental differences that have been reported in the sorption kinetics of systems catalyzed by single elements vs. that of bimetallic catalyst phases [38].

Both V and Nb are known catalysts that promote the hydrogen sorption kinetics in Mg [42–44]. They have body-centered cubic (bcc) structures, with appreciable hydrogen solubility and high hydrogen diffusivity [45]. In addition, both elements form hydrides at the pressures/temperatures utilized for magnesium. The catalytic properties of their respective hydrides, rather than those of the metals, have been suggested to play an equally important role for catalyzing the reactions under certain sorption conditions [46]. Though binary systems of Mg and a single transition metal have been the subject of extensive research, hydrogen storage in Mg-rich ternary Mg–V–Nb has not received any attention.

In the present study the interrelationship between the microstructure and the hydrogen storage cycling behavior of Mg-rich ternary Mg–V–Nb alloys is investigated in detail. As a baseline we also present the properties and the microstructure of Mg–V and Mg–Nb systems. As will be demonstrated, Mg–20 V and Mg–10 V–10 Nb samples possess similarly rapid initial hydrogen sorption kinetics. However, the two systems show fundamentally differing trends in the microstructural evolution induced by hydrogen absorption and desorption cycling, with concomitantly disparate rates of kinetics degradation. Though we utilize a variety of analytical techniques along with Avrami-type (Johnson–Mehl–Avrami; JMA) kinetic analysis, our primary tool is cryogenic stage transmission electron microscopy (TEM). Using cryo-stage TEM allowed us to observe the microstructures in the fully hydrided or fully metallic state with minimal beam-induced specimen damage. It also allowed us to examine partially sorbed microstructures containing both Mg and MgH_2, thus allowing for a realistic comparison between the obtained JMA parameters and the actual growth process. Combining these techniques led to a general mechanistic description of the microstructural evolution in these alloys both at 200 °C and at room temperature.

2. Experimental

The ternary Mg–V–Nb and binary Mg–V and Mg–Nb alloy films were synthesized by physical vapor deposition (PVD). They were 10 cm. in diameter and 1.5 μm thick. The Mg–based alloy films were coated with 7.5 nm Pd/7.5 nm Ta bi-layers on the top and bottom of the stack. The Ta interlayer reduced the rate of intermetallic formation between the Mg and the Pd, allowing the Pd to stay active during the first few cycles [47]. Deposition was performed using a DC-magnetron co-sputtering system (AJA International Inc. ATC ORION 8), in a sputter-up configuration with continuous substrate rotation. The substrate temperature was maintained near ambient for all depositions. Argon gas with a purity of 99.999% was used at a working pressure of 5×10^{-3} mbar, with a maximum base pressure of 5×10^{-8} mbar. The Si substrates were first coated with a layer of hardened photoresist to enable post deposition lift-off of the films using acetone. The deposition rates were as follows: Mg 2.3 Å s^{-1}, Pd 1.6 Å s^{-1}, Ta 0.3 Å s^{-1}. The deposition rates of V and Nb varied accordingly to adjust for different stoichiometries. The levels of secondary additions were kept the same for both ternary and binary samples, namely 20 at.%. For simplicity, we denote samples as Mg–*x* V–*y* Nb, which indicates stoichiometry of 80 at.% Mg–*x* at.% V–*y* at.% Nb.

Volumetric absorption and desorption kinetic measurements and the desorption pressure-compositions isotherms (PCT-desorption) were performed on an automated Sieverts type hydrogen sorption analysis system (Hy-Energy LLC. PCTPro 2000). The typical sample amount used for each measurement was ~15 mg. Cycling kinetics measurements were performed at 200 °C and at 20 °C. For cycling tests at 200 °C, the hydrogen pressures at the beginning of absorption and desorption steps were ~2.3 and 0.007 bar, respectively. The absorption and desorption steps were reversed when the average sorption rate fell below 0.005 wt.% min^{-1} over a period of 3 min. Room temperature hydrogen uptake was performed with a sample that first underwent 50 full sorption cycles at 200 °C. The sample was then cooled to 20 °C and absorbed at 1 bar. After absorption, the sample was again heated to 200 °C to desorb at a starting hydrogen pressure of 0.005 bar. Partially absorbed/desorbed samples were prepared by interrupting the sorption process at a predetermined reaction wt.% fraction.

X-ray diffraction (XRD) analysis was performed on a Bruker AXS diffractometer (Bruker Discover 8) using a