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Microstructural modifications induced by hydrogen absorption in Mg_5Ga_2 and Mg_6Pd

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Abstract

We have recently proposed a new method to design one-dimensional structures of MgH_2 in the nano- and micrometer ranges by hydrogen-induced disproportionation of bulk $Mg_{24}Y_5$. The present study confirms the same behavior in hydrogenated Mg_5Ga_2 and Mg_6Pd. Single-crystalline one-dimensional structures and microparticles of MgH_2 are formed by hydrogen absorption and subsequent partial disproportionation of Mg_5Ga_2 and Mg_6Pd. The MgH_2 whiskers and particles grow with different morphologies for different alloying partners. Growth mechanisms are proposed in relation to the morphology and the chemical surface composition of original compounds.

Keywords: Magnesium intermetallics; Hydride; Microstructure; Surface properties

1. Introduction

Hydrogen absorption in metals is of considerable importance for both fundamental and applied research. Many metals absorb hydrogen directly by gas–solid reaction at a specific temperature and gas pressure [1]. Hydride formation is often associated with modifications of physical properties and, in particular, the structure and microstructure. Reversible hydriding is a key point for many technological applications, such as fuel cells, hydrogen solid-state storage materials [2] and material processing by hydrogen disproportionation desorption recombination (HDDR) [3].

Magnesium can absorbs up to 7.6 wt.% hydrogen by forming MgH_2 and is considered as one of the most attractive materials for hydrogen storage. However, Mg presents serious drawbacks for the use in a robust, sustainable and long-life storage device, such as very slow kinetics and a high absorption/desorption temperature (573–673 K) [1,4]. In order to overcome these inherent limitations, two methods have been extensively investigated. One is to reduce the Mg particle size to micro- or nanorange by mechanical synthesis methods [5], the other to alloy Mg with other elements [4,6]. Recently, we have discovered a synthetic method of tailoring micro- and nanostructures of MgH_2 single crystals starting from bulk $Mg_{24}Y_5$ [7]. One-dimensional structures ("whiskers") of MgH_2 are selectively grown by hydrogen absorption and subsequent disproportionation of $Mg_{24}Y_5$. In the present study it has been shown that this behavior is also valid for Mg_5Ga_2 and Mg_6Pd.

Mg_5Ga_2 crystallizes in an orthorhombic structure with the space group Ibam [8,9]. No previous studies on hydrogen absorption properties of Mg_5Ga_2 have, to our knowledge, been reported. Mg_6Pd has a small range of homogeneity between $Mg_{5.6}Pd$ and $Mg_{6.8}Pd$ and crystallizes in a cubic phase [10,11]. The crystal structure can be described in very complex packing blocks according to the F-43m space group. The hydrogen absorption properties of Mg_6Pd have been reported previously [12]. Prior

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to the hydrogenation, these authors prepared the sample by surface treatment with tetracyanoethylene (TCNE).

2. Sample preparation and experimental details

The samples were prepared from appropriate amount of the elements: Mg of 99.95% purity (Alfa Aesar), Ga of 99.99% purity (Goodfellow) and Pd of 99.95% purity (Cerac). In order to avoid Mg loss by evaporation and contamination, pure elements were welded in a Ta crucible under Ar atmosphere. The tantalum tubes were heated either in an induction furnace (up to 1073 K) filled with 0.3 bar of Ar or a resistance furnace (up to 773 K) evacuated at a base pressure of 10^{-9} bar. No reaction between the tantalum crucibles and the molten compound could be seen. The samples were handled inside a glove box under Ar atmosphere.

Hydrogenation syntheses were performed in an autoclave system at different pressures and temperatures. Prior to hydrogenation, the system was evacuated to a base pressure of 10^{-5} bar and flushed several times with hydrogen gas. The samples were loaded directly from the glove box to the autoclave without exposure to air. The hydrides were prepared by repeating 2–3 heat-treatments at given applied hydrogen pressures. No surface treatment was performed prior to hydrogenation.

X-ray diffraction (XRD) measurements were carried out on powder samples using a Guinier–Hägg camera with Cu Kα_1 radiation and Si as internal standard.

Chemical surface analyses were performed by X-ray photoelectron spectroscopy (XPS) measurements using a Phi Quantum 2000 instrument with a monochromatic Al Kα source of 1486.6 eV, at room temperature with a base pressure in the main chamber lower than 10^{-11} bar. The surface and bulk chemical compositions at different depths were determined by bombarding selected areas of the samples with Ar$^+$ and sequentially analyzed. The total sputtering time for the depth profile was maximum 11 min.

Microstructural and chemical analyses were performed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) techniques before and after hydrogenation. SEM investigations were carried out using a high-resolution LEO 1550 microscope equipped with an in-lens detector. The preparations of the specimens for SEM investigations were made by dispersing the powder materials on a carbon tape.

Prior to the XRD, XPS, SEM and EDS measurements, the specimens were exposed to air.

3. Results and discussions

3.1. Starting compounds

The X-ray powder diffraction patterns confirmed that the Mg_5Ga_2 and Mg_6Pd samples were single phased, crystallizing in the orthorhombic Ibam and cubic F-43m space groups, respectively. The lattice parameters were $a = 7.028(1)$ Å, $b = 13.729(2)$ Å and $c = 6.031(1)$ Å for Mg_5Ga_2 and $a = 20.053(5)$ Å for Mg_6Pd. These results are in good agreement with previously reported values [9,11].

The chemical composition of the surface was determined by XPS measurements before hydrogen exposure. Elemental depth profile analysis was carried out through hundreds of atomic layers into the bulk material by Ar$^+$ sputtering. The investigated XPS electronic levels were Mg 2p, O 1s, Ga 2p and/or Pd 3d. The evolutions of the Mg 2p, Ga 2p and/or Pd 3d peaks with the sputtering time are shown in Figs. 1 and 2 for Mg_5Ga_2 and Mg_6Pd, respectively.

The surface layer of both samples is partially composed by oxidized Mg atoms. The oxidized Mg 2p peaks are shifted towards higher binding energy (Figs. 1 and 2) and completely disappears after approximately 1 min of Ar$^+$ sputtering, which is in agreement with the O 1s peak evolution. In the case of the Mg_5Ga_2 compound, the broad Mg 2p peak for low sputtering times indicates a large overlap of the XPS signals from both oxidized and metallic Mg atoms (Fig. 1). The Ga or Pd atoms are found exclusively

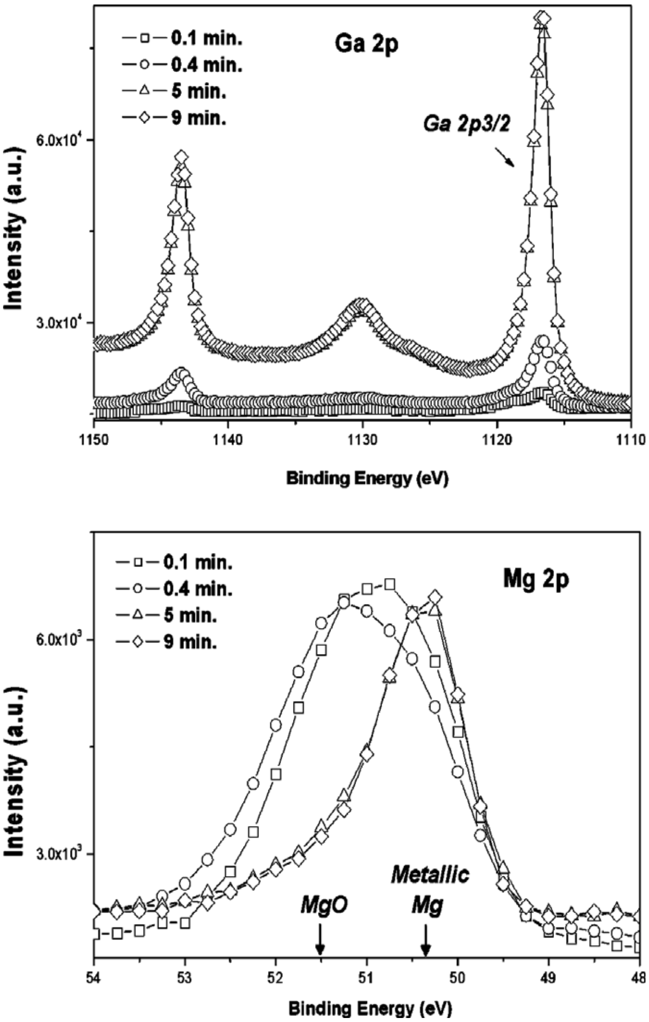

Fig. 1. XPS profiles of the Ga 2p and Mg 2p electronic levels of the Mg_5Ga_2 compound for different Ar$^+$ sputtering times.