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Formation of metastable phases in magnesium–titanium system by high-pressure torsion and their hydrogen storage performance

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ABSTRACT

No binary phases exist in the Mg–Ti binary equilibrium phase diagram and the two elements are totally immiscible even in liquid form. This study shows that four metastable phases (two with the bcc and fcc structures and two with the hcp structures) are formed in the Mg–Ti system by severe plastic deformation (SPD) through the process of high-pressure torsion (HPT). Investigation of hydrogenation properties reveals that these metastable phases are decomposed to pure Mg and Ti during heating before they can absorb the hydrogen in the form of ternary Mg–Ti hydrides. First-principles calculations show that the hydrogenation reaction should occur thermodynamically, and ternary Mg–Ti hydrides with the cubic structure should form at low temperature. However, the slow kinetics for this reaction appears to be the limiting step. Calculations show that the binding energy of hydrogen increases and the thermodynamic stability of hydrides undesirably increases by addition of Ti to Mg.

1. Introduction

Mg and Ti, which are considered as two light metals, are the 7th and 9th most abundant elements in the earth's crust. Since both elements react with hydrogen and produce hydrides of MgH_2 and TiH_2 (with hydrogen contents of 7.6 and 4.0 wt.%, respectively), they are considered as candidates for hydrogen storage. However, both MgH_2 and TiH_2 hydrides are stable and they desorb hydrogen only at elevated temperature [1]. For hydrogen storage applications, it is an important issue to identify strategies to reduce the dehydrogenation temperatures of hydrides [2].

The addition of other elements to Mg and Ti is one approach to reduce the binding energy with hydrogen and decrease the dehydrogenation temperature [3]. However, the elemental additives should be mixed with Mg and Ti at the atomic scale (alloys should form), i.e., ternary or complex hydrides should be formed in the presence of hydrogen [1,3]. For example, ternary hydrides Mg_2NiH_4 [4] and $TiFeH_2$ [5] exhibit lower dehydrogenation temperatures than MgH_2 and TiH_2. Although $TiFeH_2$ desorbs hydrogen at room temperature [4], Mg-based hydrides such as Mg_2NiH_4 usually desorb the hydrogen only at elevated temperatures [1,6].

Several earlier works suggested that Ti can be a promising additive to Mg to form hydrides with lower stability [7–11]. However, atomic-scale mixing of Mg with Ti is thermodynamically impossible, as no binary phases are formed in the Mg–Ti equilibrium phase diagram even in liquid form [12]. Several groups employed special techniques such as sputtering [13], electron beam deposition [14] and physical vapor deposition [15], and reported that alloying of Mg and Ti does not occur even in the non-equilibrium conditions. Formation of metastable phases in the Mg–Ti system during ball milling was first reported by Tsuchio et al. [16]. Liang and Schulz found that supersaturation of Mg in Ti occurs by mechanical alloying of Mg/Ti blends using ball milling [17]. Borsa et al. reported that a Mg–Ti alloy with the hcp structure is formed by co-sputtering of Mg and Ti in Ar atmosphere [18]. Asano et al. [19–21], Rousselot et al. [22], Calmak et al. [23] and Maveja et al. [24] reported that several metastable phases with bcc, fcc and hcp structures are formed in the Mg–Ti system by application of high-energy ball milling to Mg and Ti powders in Ar atmosphere.

Although the formation of metastable phases has been reported in ball-milled powders and in thin films, it is important to determine whether these binary phases can be formed in bulk samples of high-purity Mg–Ti mixtures using other techniques. Processing of Mg–Ti through severe plastic deformation (SPD) techniques [25,26] can be an approach to synthesize bulk samples of Mg–Ti alloys. The SPD techniques are not only free from contamination,

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but they also are quite effective for enhancing atomic diffusion [27,28], mixing elements at the atomic scale [29–31], synthesizing intermetallics [32], enhancing phase transformations [33–35] and improving hydrogen storage properties [36–42].

In this study, an SPD technique, known as high-pressure torsion (HPT) [43,44], is employed for atomic-scale mixing of Mg and Ti to form bulk samples of Mg_2Ti. Hydrogen storage properties of the material are investigated experimentally, and the effect of Ti addition on the thermodynamical stability of Mg–Ti hydrides is studied by using density functional theory (DFT).

2. Experimental materials and methods

Pure Mg (99.9%) powders with particle sizes of <180 μm were mixed by mechanical agitation with 33.3 mol% Ti (99.99%) powders with particle sizes of 39–90 μm. A small amount of powder (<1 g) was placed between two Bridgman anvils [45] under a pressure of $P = 3$ GPa, and intense shear strain ($\gamma = 2\pi r N/h$, γ: shear strain, r: distance from disc center, N: number of turns, h: disc thickness [25,26]) was introduced by rotating the two anvils with respect to each other for $N = 100$ turns (in air atmosphere and room temperature). The material had a disc shape with 14 mm diameter and 0.8 mm thickness after HPT processing.

The HPT-processed discs were first examined by X-ray diffraction (XRD) using Cu Kα radiation. In order to investigate the formation of metastable phases and calculate their lattice parameters, the XRD patterns were analyzed by Rietveld method using FullProf Suite software [46,47].

For transmission electron microscopy (TEM), thin samples were prepared from the discs 6 mm away from the disc center with a focused-ion-beam (FIB) system, followed by ion milling and plasma trimming. TEM was performed at either 200, 300 or 400 keV for microstructure observation and for recording selected-area electron diffraction (SAED) patterns.

For examination of hydrogenation properties, samples were subjected to differential scanning calorimetry (DSC) at 25–500 °C with a heating/cooling rate of 5°/min under a hydrogen pressure of 2 MPa. After the end of DSC cooling, the samples were examined by thermogravimetry (TG) analysis at 25–500 °C with a heating/cooling rate of 5°/min under a He flow at 0.1 MPa.

3 Calculation methods

For first-principles calculations, the all-electron basis projector-augmented-wave (PAW) method [48] was used in the framework of DFT using VASP (Vienna Ab-initio Simulation Package) code [49,50] within the generalized gradient approximation in the Perdew–Burke–Ernzerhof form [51]. A plane-wave energy cut-off of 600 eV was applied for the calculations.

The calculations were first performed for MgH_2 with the tetragonal (rutile) structure in which hydrogen atoms were located in triangular sites by considering the full occupancy of these sites. Second, TiH_2 with the cubic (fluorite) structure was constructed by considering the full occupancy of tetrahedral sites by hydrogen atoms. Third, in order to examine the effect of Ti addition on the stability of $Mg_xTi_yH_{2(x+y)}$ hydrides, MgH_2, $MgTiH_4$ and TiH_2 with the tetragonal structure, and MgH_2, Mg_3TiH_8, $MgTiH_4$, $MgTi_3H_8$ and TiH_2 with the cubic structure, were constructed. The hydrogen atoms were located in the triangular and tetrahedral sites for the tetragonal and cubic structures, respectively, by using full occupancy and by considering the Switendick and Westlake criteria [52,53]. The structural forces were minimized in the hydride structures by relaxing the cell parameters and atomic positions, while the initial symmetry of the structure was kept. The Brillouin zones

were modeled using $8 \times 8 \times 12$ and $10 \times 10 \times 10$ meshes for the tetragonal and cubic structures.

The binding energy of hydrogen, E_H, was calculated as:

$$E_H = E_0 - (E_1 + 0.5E_{H-H}) \tag{1}$$

where E_0 is the energy of hydride, E_1 is the energy of hydride after removing one hydrogen atom (without allowing the structure to be relaxed) and E_{H-H} is the energy of one hydrogen molecule in the hydride unit cell. The enthalpy of formation of $Mg_xTi_yH_{2(x+y)}$ hydrides, ΔH_F, was calculated as:

$$\Delta H_F = E_0 - (xE_{Mg} + yE_{Ti} + E_{H-H}) \tag{2}$$

where E_{Mg} and E_{Ti} are the energy of Mg and Ti atoms in the unit cell. The charge density difference, C_H, was calculated as:

$$C_H = C_0 - \left(C_1 + C_H^0\right) \tag{3}$$

where C_0 is the total charge density distribution in the hydride, C_1 is the charge density after removing one hydrogen atom and C_H^0 is the charge density of hydrogen atom located in the same position as the removed hydrogen atom in the hydride unit cell. Bader population analysis [54] was performed to allocate electron density and a VESTA program was used for 3D visualization of the electron density [55,56]. In order to understand the interaction of hydrogen atoms with Mg and Ti atoms, the electronic structures of the hydrides were calculated in the form of total and partial density of states (DOS).

4. Results and discussion

XRD profiles for the Mg/Ti powder mixtures and for the Mg/Ti disc samples processed by HPT for 100 turns are shown in Fig. 1. For the HPT-processed discs, the XRD analyses were conducted at the mid-radii of the disc (less-strained region with $\gamma = 2700$) and at the disc edge disc (highly-strained region with $\gamma = 4700$). Since texture is developed during the HPT processing, the disc edge was crushed and re-examined by XRD analysis. An examination of Fig. 1 indicates that several phases form after HPT processing of the powders. While peaks for Mg and Ti are still visible at the mid-radii of disc, they totally disappear at the disc edge.

The presence of different phases after HPT processing is shown more clearly in the XRD pattern obtained after crushing the disc. Rietveld analysis suggests that four metastable phases are formed: (i) bcc with $a = 0.345$ nm; (ii) fcc with $a = 0.429$ nm; (iii) hcp with $a = 0.319$ nm and $c = 0.517$ nm (hereafter, called hcp-I); and (iv) hcp with $a = 0.297$ nm and $c = 0.514$ nm (hereafter, called hcp-II). Fig. 1 also shows that significant peak broadening occurs due to straining through the HPT process, indicating the occurrence of
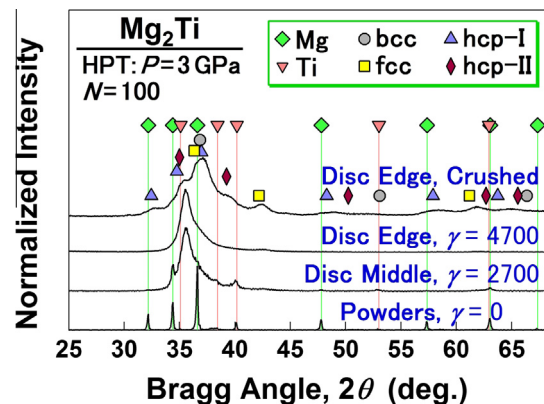

Fig. 1. XRD profiles for Mg – 33.3 mol% Ti sample processed by HPT taken from mid-radii of disc and edge of disc (with and without crushing) including profile for Mg/Ti powder mixtures.