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New FCC Mg–Zr and Mg–Zr–ti deuterides obtained by reactive milling

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ABSTRACT

Results for binary Mg–Zr and ternary Mg–Zr–Ti mixtures ball milled at room temperature under reactive deuterium atmosphere (5.6–6.7 MPa) are reported. X-ray and neutron powder diffraction combined with Rietveld refinements show that two new cubic phases were formed during milling. $Mg_{0.40}Zr_{0.60}D_{1.78}$ and $Mg_{0.40}Zr_{0.26}Ti_{0.34}D_{1.98}$ crystallize with disordered face centered cubic metal atom arrangements. Results of differential scanning calorimetry and termogravimetric measurements demonstrate that both deuterides desorb deuterium at lower temperatures than MgD_2, ZrD_2 or TiD_2; 528 and 575 K in the Mg–Zr–D and Mg–Zr–Ti–D system, respectively. Interestingly, $Mg_{0.40}Zr_{0.26}Ti_{0.34}D_{1.98}$ stores deuterium reversibly at 673 K and 10 MPa of D_2.

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1. Introduction

Optimized, commercial hydrogen storage systems based on lightweight magnesium hydride are mainly dedicated to stationary energy storage applications [1], while on-board and small volumetric hydrogen storage solutions for portable devices are still challenging. MgH_2 contains 7.6 wt% of hydrogen, which makes it an attractive compound for hydrogen storage applications. However, the high thermal stability and slow kinetics of its rutile-type structure significantly hinder its widespread use in commercial energy storage systems. Many factors such as a chemical composition [2–4], an addition of catalytic species [5–10], processing technologies [5,11–14] and microstructural parameters, particularly grain size [6,15–17], have an effect on the hydrogen storage capacity, kinetics and/or thermodynamics of Mg-based intermetallic compounds. Conventional crystalline alloys often suffer from relatively slow hydrogen sorption kinetics even at high temperatures, while nanocrystalline and amorphous materials exhibit much faster kinetics at lower temperatures, as their large number of interfaces, defects and grain boundaries, provide easy pathways for hydrogen diffusion [18–21]. Their wider use is however limited by the poor reversibility at ambient temperature and pressure. In recent years, many investigations have therefore explored different ways that could efficiently reduce the hydrogen sorption temperatures and improve the reversibility of Mg-based metal hydrides. Several approaches, e.g. elemental substitutions [22–26], mechanical alloying [22,25,27] and high-pressure synthesis [28], have been applied separately or jointly resulting in a formation of a number of improved and promising compounds but none of them reveal outstanding kinetic or/and thermodynamic properties. Novel Mg–TM hydrides (TM = transition metal) have been previously obtained from MgH_2 and different TM or TM hydrides in an anvil cell under mechanical pressure of several GPa [29]. This technique was successfully used for Mg-based hydrides with Hf [28,30,31], Nb [28,31–34], Mo [34], Ta [28,30,31], Ti [28,29,35], V [28] and Zr [28,30,31,34,36]. All compounds, except a fully disordered Zr-containing phase, crystallize with face-centered cubic (FCC) metal atom arrangement that can be described as Ca_7Ge-type structure with hydrogen atoms located in two different tetrahedral sites [28] and references therein. The presence of the TM atoms helps to retain the cubic structure of hydrides when releasing the high pressure down to ambient. Unfortunately, upon heating, most of the resulting Mg-TM hydrides decompose to binary hydrides releasing gaseous hydrogen at temperatures 100–150 K below pure MgH_2 [30,32,33,37]. Formation of monoclinic phases, e. g. $Mg_{0.33}Zr_{0.67}H_{\sim 2}$ and $Mg_{0.33}Nb_{0.67}H_{\sim 2}$, which are thermally more stable than cubic ones, have also been reported for certain TMs (Nb, Zr, Hf and Ta) [31]. $Mg_{0.82}Zr_{0.18}H_2$ obtained at high pressure can reversibly release ~3.0–3.5 wt% of H_2 (i.e. 60–70% of the total hydrogen content) at 523 K [36]. The FCC structure of the hydride is preserved due to remaining hydrogen, which most likely stabilizes the metastable phase [30,36]. The same behavior has been reported for disorder FCC Ti-containing Mg-based hydrides [23,24]. In spite of being

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thermodynamically immiscible, extended solubility of Mg in Ti and vice versa has been achieved by mechanical milling [38–40] and references therein. It has been reported that $Mg_{1-y}Ti_y$ intermetallic compounds ($0.2 < y < 0.65$) can crystallize either with FCC, body-centered cubic (BCC) or hexagonal close-packed (HCP) structure depending on the elemental composition of the starting mixture as well as the dynamic energy delivered by the milling media [41]. Partial substitution of Mg atoms by Ti atoms is expected to preserve the cubic structure of Mg–Ti hydride during hydrogen cycling and decrease sorption temperature. Single Mg–Ti–H phase with up to 4.0 wt% of H_2 can be formed from mechanically alloyed powder at 423 K under 8 MPa of hydrogen gas [42,43]. However, hydrogenation of Ti/Mg solid solutions at 563 K can result in their decomposition to MgH_2 and TiH_2 [44,45]. In this paper we focus on alloying Mg–Zr and Mg–Zr–Ti powder mixtures under deuterium gas and report on the synthesis, structural characterization and thermal stability of deuterides obtained by reactive ball milling. The results are compared to published data for Mg–Zr hydrides [36] obtained by high-pressure synthesis. Single-phase deuterides in the Mg–Zr–Ti system have not been reported previously.

2. Synthesis and characterization

Elemental powder mixtures with nominal composition $Mg_{0.45}Zr_{0.55}$ and $Mg_{0.45}Zr_{0.25}Ti_{0.30}$ (all metals purchased from Alfa Aesar, purity of 99% or better), were ball milled under a reactive atmosphere of deuterium gas, 5.6 and 6.7 MPa, respectively, in a commercial vial from evicomagnetics [46]. This specially designed hardened steel vial, equipped with pressure and temperature sensors, is compatible with the Fritsch P6 planetary ball mill. Milling was carried out at 450 rpm for 24 h with ball-to-powder weight ratio of 40:1. Deuterium gas was used instead of natural hydrogen for powder neutron diffraction (PND) experiments. The powders were handled in a glove box under protective Ar atmosphere (<0.1 ppm O_2 and H_2O). The as-milled powders were analyzed by both high resolution synchrotron powder X-ray diffraction (SR-PXD) as well as PND. SR-PXD measurements were performed at the Swiss-Norwegian beam line (SNBL), ESRF (Grenoble, France), at the BM01B station. The wavelengths for the experiments where: $\lambda=0.50350$ and 0.50462 Å. In all SR-PXD experiments the powders were sealed in boron-glass capillaries ($d=0.3$ mm). PND data were collected with the PUS diffractometer ($\lambda=1.5557$ Å) at the JEEP II reactor (Kjeller, Norway). The samples were loaded into 6 mm vanadium container and sealed with indium wire. Rietveld refinements were performed with the software *FULLPROF* [47]. X-ray scattering factors and neutron cross-sections were taken from the *FULLPROF* library. The SR-PXD backgrounds were modeled by Chebyshev polynomials, while 12-coefficient Fourier-cosine polynomial was used to fit the background in the PND data. In both cases Fourier filtering procedure was applied at the final stages of the refinements. Pseudo-Voigt profile function was used to model the Bragg peak shapes. Deuterium desorption was investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TG) and temperature programmed desorption (TPD). DSC and TG measurements were carried out using *NETSCH* STA449C Jupiter instrument at 5 K/min in argon flow (50 ml/min). TPD experiments were performed in an in-house built setup and carried out under dynamic vacuum using heating rates of 5 K/min. Gas desorption was detected as a temporary increase of the pressure in the system. Elemental analysis was performed in the Hitachi S-4800 scanning electron microscope (SEM) equipped with the Noran System Six energy dispersive spectrometer (EDS). Absorption/desorption experiments were performed using an in-house built Sieverts apparatus equipped with a pressure sensor from Presens [48] operable up to 20 MPa and 773 K.

3. Results

3.1. Synthesis by reactive milling

Fig. 1 presents the changes of pressure and temperature during ball milling of 0.45 Mg+0.55 Zr and 0.45 Mg+0.25 Zr+0.30 Ti (molar ratio) powder mixtures in D_2 atmosphere. In both cases the temperature increases sharply in the early stage of the milling and reaches a value of 320 K after 3 h. Such behavior is typical for planetary ball milling and results from the impact and attrition of the balls on the internal walls of the vial. For both mixtures, a significant increase of pressure at the beginning of milling is also observed, which is consistent with the temperature rise. A decrease of the pressure is recorded after approx. 100 and 15 min of milling for Mg–Zr and Mg–Zr–Ti mixture, respectively, and can be assigned to the onset of deuterium absorption. The formation of deuterated phases, induced by the mechanical transformation, occurs in one step and is significantly faster in the Ti-containing sample. A small hump appearing on the pressure curve between 4 and 5 h of milling in Mg–Zr–D system is most likely related to the observed temperature variation. The influence of Ti content in the ball milled mixture on the kinetics of hydrogen absorption reaction has already been reported [17,38–40,49–52]. Since the reaction appears to proceed in a single step, it seems unlikely that formation of TiD_2 as intermediate product is the cause of accelerated formation of the final deuteride. However, the abrasive role of the possible Ti–D-based phase that can promote deuterium uptake in Mg–Zr powder cannot be excluded [38–40]. After 4 and 2 h of milling the deuterium absorption

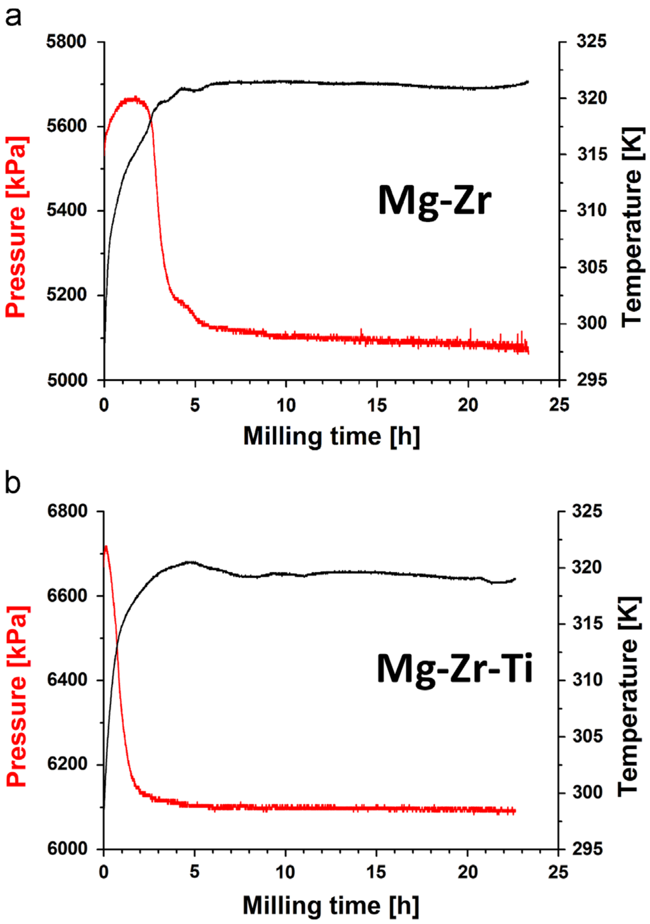

Fig. 1. Pressure (red) and temperature (black) inside the vial plotted as a function of the milling time for Mg–Zr (a) and Mg–Zr–Ti (b) powder mixtures ball milled in a reactive deuterium atmosphere. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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