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Ternary compounds in the magnesium–titanium hydrogen storage system

Dmytro Korablou^a, Flemming Besenbacher^b, Torben R. Jensen^{a,*}

^a Center for Materials Crystallography (CMC), Interdisciplinary Nanoscience Center (iNANO), Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark

^b Interdisciplinary Nanoscience Center (iNANO) and Department of Physics and Astronomy, Aarhus University, Ny Munkegade 120, DK-8000 Aarhus C, Denmark

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ABSTRACT

Mg–Ti–H samples were mechano-chemically synthesized by ball milling in argon atmosphere or under elevated hydrogen pressure. The detailed reaction mechanism during hydrogen release and uptake during continuous cycling was investigated by *in-situ* synchrotron radiation powder X-ray diffraction (SR-PXD) experiments. The thermal behaviour of the samples and hydrogen desorption properties were examined by simultaneous thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and mass spectrometry (MS) measurements. A ternary Ti–Mg–H compound with a fcc lattice form during mechano-chemical sample preparation in hydrogen atmosphere using metal powders, but not using metal hydrides as reactants. The amount of β -MgH₂ increases during the first hydrogen absorption cycle at 300 °C at the expense of the high-pressure polymorph, γ -MgH₂ and the amount of β -MgH₂ remain constant during the following hydrogenations. This study reveals that the ternary compound tends to absorb increasing amounts of magnesium in the dehydrogenated state during cycling. A strong coupling between the amounts of magnesium in the ternary Ti–Mg–H phase and the formation of magnesium and magnesium hydride during hydrogen release and uptake at 300 °C is observed. The composition and the amount of the Ti–Mg–H phase appear to be similar in the hydrogenated state. Fast absorption–desorption kinetics at 300 °C and lower onset temperatures for hydrogen release is observed for all investigated samples (lowest onset temperature of desorption $T_{on} = 217$ °C).

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Introduction

Magnesium and magnesium-based hydrides are attractive candidates as reversible hydrogen storage materials, in particular for stationary applications, owing to their high

gravimetric and volumetric capacities (up to 7.6 wt% H₂ and 109 g H₂ L^{−1}, respectively), cyclic reversibility and low costs [1–4]. Virtually limitless amounts of magnesium are available, i.e. 0.13 wt% in sea water and 2.76 wt% in the earth crust. Unfortunately, utilization of magnesium based hydrogen storage materials for mobile applications is hampered by

* Corresponding author. Tel.: +45 8942 3894; fax: +45 8619 6199.

E-mail address: trj@chem.au.dk (T.R. Jensen).

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Table 1 – Composition of the Mg–Ti–H samples prepared mechano-chemically.

	Notation	Reactants	Composition [mol%]		Ball milling conditions time [min]/gas/p(gas) [MPa]	Composition after RBM
			Mg/MgH ₂	Ti/TiH ₂		
S1	0.9Mg–0.1Ti	Mg, Ti	90/0	10/0	180/H ₂ /8	β-MgH ₂ , γ-MgH ₂ , TiH ₂
S2	0.7Mg–0.3Ti	Mg, Ti	70/0	30/0	180/H ₂ /8	fcc, β-MgH ₂ , γ-MgH ₂
S3	0.5Mg–0.5Ti	Mg, Ti	50/0	50/0	180/H ₂ /8	fcc
S4	TiH ₂	Ti	0/0	100/0	180/H ₂ /8	TiH ₂
S5	MgH ₂	MgH ₂	0/100	0/0	60/Ar/0.1	β-MgH ₂ , γ-MgH ₂
S6	0.8MgH ₂ –0.2TiH ₂	MgH ₂ , TiH ₂	0/80	0/20	60/Ar/0.1	β-MgH ₂ , γ-MgH ₂ , TiH ₂
S7	0.8TiH ₂ –0.2Mg	TiH ₂ , Mg	20/0	0/80	60/Ar/0.1	TiH ₂ , Mg

unfavourable thermodynamics, i.e. $\Delta H \sim 75$ kJ/mol and $\Delta S \sim 135$ J/Kmol [5].

Several different approaches have been explored in order to improve thermodynamics and kinetics for hydrogen release and uptake in magnesium hydride, e.g. nanoconfinement [5–9], nanostructuring by ball milling [10], utilization of catalytic additives [11,12] or alloying with transition metals [13–20]. Nanoconfinement may slightly improve thermodynamics for particle sizes less than ~ 5 nm [6–9] but is often found to provide significant improvement of kinetic properties [21,22]. Mechanochemical treatment, i.e. ball milling, can introduce nanostructuring and decreasing of both particle size and the grain size of MgH₂ powders, which significantly improve the hydrogen kinetics even for short processing in a high-energy ball mill [23,24]. Reactive ball milling (RBM) under elevated hydrogen pressure is useful for the formation of nanograins, which can take place simultaneously with the formation of a hydride [10,25].

Composites formed by magnesium and the lightest transition metal, titanium, have received significant attention as possible hydrogen storage materials. However, Mg–Ti alloys cannot be obtained by conventional technologies [26], because magnesium and titanium are thermodynamically immiscible due to a positive enthalpy of mixing ($\Delta H_{\text{mix}} > 20$ kJ/mol) [27]. The boiling point of Mg (1091 °C) is lower than the melting point of Ti (1668 °C), which hamper their alloying by melt mixing techniques. In contrast, Mg–Ti–H alloys can be produced, e.g., in the form of thin films by electron beam deposition, physical vapour deposition and magnetron co-sputtering [26–39].

Several new Mg_xTH_y (T = Ti, V, Cr, Mn, or Nb) compounds have been prepared by mixing MgH₂ with a transition metal or binary transition metal hydride and heating in high hydrogen pressure at a GPa level [40–43]. It was reported that the temperature of hydrogen desorption from Mg₇TiH_xfcc hydride was lower than that of MgH₂ and TiH_{1.9} hydrides.

All above mentioned synthesis methods are energy consuming, relatively expensive and difficult to adapt to large scale production of low cost powdered Mg–Ti–H materials for hydrogen storage applications. In this context, RBM is a very convenient and efficient synthesis approach [10] to form a large variety of equilibrium and non-equilibrium materials at room temperature, starting from elemental, pre-alloyed or hydrided Mg and Ti powders [44–54]. Our preliminary studies [53,54] have shown that Mg–Ti alloys with 30–40 mol% of Ti revealed improved hydrogen release and uptake properties as compared to MgH₂ possibly due to synergetic effects from multiphase composites consisting of γ-MgH₂, β-MgH₂ and

cubic Ti–Mg–H. Previously, the latter was suggested to form by Ti insertion in MgH₂ [55], but later by Mg insertion in fast-formed TiH₂ [52,53]. Reactive ball milling of equimolar Mg and Ti metal mixture forms a single-phase fcc structure, which is confirmed by powder X-ray diffraction (PXRD) and differential scanning calorimetry [52,53]. However, Rietveld refinement of PXD data later revealed that the synthesized material was in fact a nanocomposite consisting of β-, γ-MgH₂, ε-TiH₂, and no ternary hydrides were observed [3]. In some investigations of reactive ball milled samples of MgH₂-TiH₂ (at $p(\text{H}_2) = 13.8$ MPa) similarly did not provide any evidence for formation of ternary compounds [56], as well as at $p(\text{H}_2) = 30$ MPa [57], in contrast to other, where RBM of MgH₂-TiH₂, MgH₂-Ti or TiH₂-Mg powder provided new fcc compounds with lattice parameters 4.47 and 4.25 Å depending on the hydrogen content [58]. Moreover, several ternary Mg–Ti–H compounds have been synthesized applying RBM and characterized [50–52].

Clearly, there exists a controversy in the literature regarding ternary compounds formed in the Mg–Ti–H hydrogen storage system and their role in the mechanism for hydrogen release and uptake. This has prompted the present investigation using reactive ball milling (RBM) for synthesis and nanostructuring of Mg–Ti–H samples and in-situ synchrotron radiation powder X-ray diffraction, thermal analysis coupled with mass spectrometry for detailed characterization of the mechanism for dehydrogenation and hydrogenation.

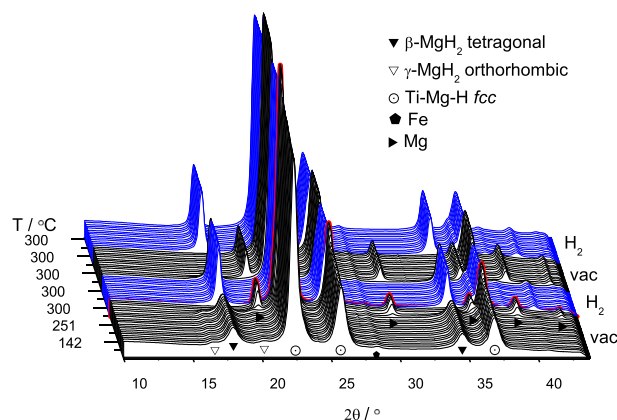


Fig. 1 – In-situ SR-PXD data measured for sample S2 (0.7Mg–0.3Ti) heated from RT to 300 °C (5 °C/min) in vacuum and subsequently cycled at this temperature applying alternately $p(\text{H}_2) = 8$ MPa and vacuum ($\lambda = 0.997495$ Å).

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