

## HYDROGENATION PROPERTIES OF BALL-MILLED Mg-Ti-C-Zr COMPOSITE

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### Abstract

The hydrogen storage properties of ball-milled Mg-Ti-Zr-C composite (1.8 wt.% Ti, 1.9 wt.% Zr and 0.2 wt.% C) were investigated. It has been previously shown, that the addition of Ti, Zr and C improved its storage properties. This beneficial effect of additives upon hydrogen storage properties can be explained by catalysis by the particles rich in Ti or Zr located on the surface of Mg grains. They provide effective pathways for the hydrogen diffusion into the MgH<sub>2</sub>. The morphological and microstructural characteristics were investigated by scanning electron microscopy and by X-ray diffraction. The hydrogen sorption was measured by Sieverts method using Setaram PCT-Pro device. In this paper, sorption behaviour of the composite after ball-milling and after aging on the air was compared. The ball-milled composite adsorbed 3.5 wt.% H<sub>2</sub> within 10 min at 623 K. However, hydrogen storage capacity of the composite aged on the air for 7 months remarkably decreased: The aged composite adsorbed within 10 min only 2 wt.% H<sub>2</sub> at 623 K and the sorption capacity decreased from 4.7 wt.% H<sub>2</sub> to 2.1 wt.% H<sub>2</sub>.

**Keywords:** Hydrides, hydrogen storage, catalysis, hydrogen, Mg-alloys

### 1. INTRODUCTION

Recently, a lot of Mg based materials were studied, but only sparse examples of promising candidates for hydrogen storage can be found in literature. One class of prospective alloys are Mg-Ti based materials doped by useful catalysts, which showed relative good sorption properties.

The strong catalytic effect of nanolayers of Ti/Pd or Al was found in new nanolayered materials Ti/Mg/Ti/Pd [1] and Mg-AlTi [2]. The multilayered Mg-AlTi material (34 nm Mg and 2 nm AlTi) shows a good hydrogen sorption cycles stability and remarkable kinetics. The network structure of precipitated AlTi nano-particles would act as a barrier to boundary motion and limit the formation of large isolated pure Mg particles which lower the sorption performance of the material. This exceptional behaviour of AlTi can be well explained by diffusion rate of hydrogen that is much faster in AlTi than in Mg [2]. This causes rapid hydrogenation of Mg through the network of AlTi nanoparticles and also AlTi layers. More interestingly, the 2 nm AlTi is not affected by hydrogen since it has negligible affinity to hydrogen and can remain intact during cycling, sustaining its catalytic activity and mechanical integrity. Very promising system is also Mg-Ge-Ti, where the dehydrogenation can start at very low temperature 130 °C [3]. The addition of TiC nanoparticle led to a pronounced improvement in the de/hydrogenation kinetics of MgH<sub>2</sub> in MgH<sub>2</sub>-10 wt.% TiC. The improved hydrogen storage properties were ascribed to the TiC particles embedded in the MgH<sub>2</sub>, which provided the pathways for the hydrogen diffusion into this composite [4]. However, catalyst based on Ti is also useful in other promising hydrogen storage materials. For example, homogeneously dispersed TiC nanoparticles act as a surface catalyst on the Li-alanate and also improves hydrogen sorption properties [5].

Other very effective catalyst added to Mg-based materials is carbon, including graphite, activated carbon, carbon black, fullerene and single-walled carbon nanotubes (SWCNT) [6]. In paper [7], hydrogen desorption kinetics of hydrided Mg-Ni-In-C ball-milled alloys was investigated. It was observed that carbon improves the hydrogen desorption kinetics significantly. Its beneficial effect was found to be optimum close to the carbon

concentration of about  $cC \cong 5$  wt.%. With this composition, stored hydrogen can be desorbed readily at temperatures down to about 485 K, immediately after hydrogen charging. This can substantially shorten the hydrogen charging/discharging cycle of storage tanks using Mg-Ni-based alloys as hydrogen storage medium. For higher carbon concentrations, unwanted phases precipitated those result in deceleration of hydrogen desorption and lower hydrogen storage capacity. Recently, it was shown, that ZrO<sub>2</sub> and SWCNT co-addition can act also as an effective catalysts [8].

In this paper sorption properties in composite of Mg which contains Ti, Zr and C as catalysts were studied after ball-milling and ageing for 7 months in the air.

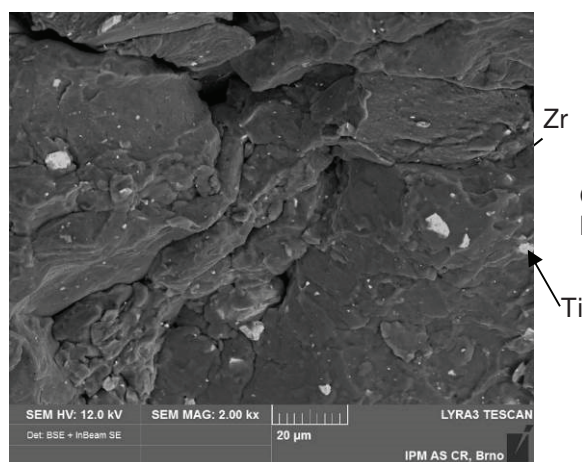
## 2. EXPERIMENTAL

The composite was ball-milled from pure components (splinters of 3N8 Mg, 3N6 Ti, 5N Zr and spectroscopic pure C powder) using the ball-mill *Fritsch-Pulverisette6* (400 rpm, 10 min milling / 50 min cooling - repeated 10 times; the mass ratio of the balls to the charge was about 60). The powder was compacted at room temperature into pellets with diameter 20 mm × 2 mm in height.

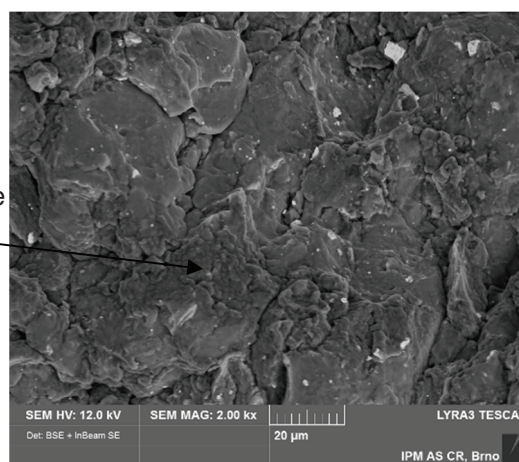
The average composition of experimental composite Mg-1.8Ti-1.9Zr-0.2C (wt.%) was measured by SEM Jeol JSM 6460 equipped with EDAX/WEDAX Oxford Instruments analyzers. The WD (wave-dispersion) analyse was used for measurement of carbon content in composite. The observation of structure and others chemical analyses was done in SEM Tescan LYRA 3 XMU FEG/SEMxFIB equipped with X-Max80 EDS detector for X-ray microanalysis.

Hydrogen sorption characteristics were measured using the Sieverts-type gas sorption analyser *PCT-Pro Setaram Instrumentation* in the present work. This equipment enables safe and fully-automated repeated measurements in both absorption and desorption regimes. The study was carried out at temperature 350 °C and under hydrogen pressure from 0.1 Pa to 2.7 MPa. The purity of both the hydrogen and helium (calibration gas) was 6N. The hydrogen was dosed using calibrated volumes corrected to dead volumes at each individual test temperature.

X-ray powder diffraction (XRD) was performed using CuK $\alpha$ <sub>1,2</sub> radiation. HighScore Plus software HighScore Plus software and JCPDS PDF-4 was used for qualitative analysis and Rietveld refinements using external LaB<sub>6</sub> standard and structural models based on the ICSD database for quantitative analysis.



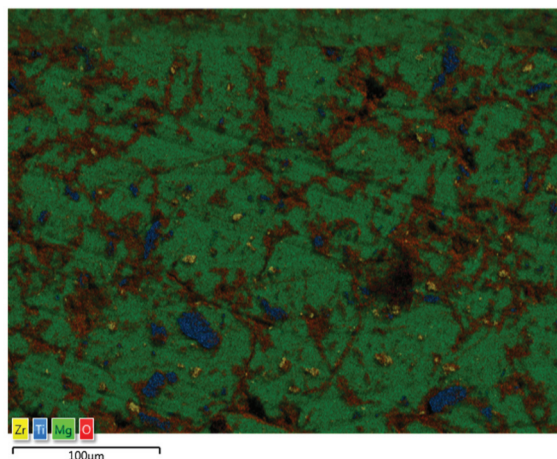
**Figure 1** Structure of b-sample, broken surface.  
Bright particles - Zr, gray particles – Ti.



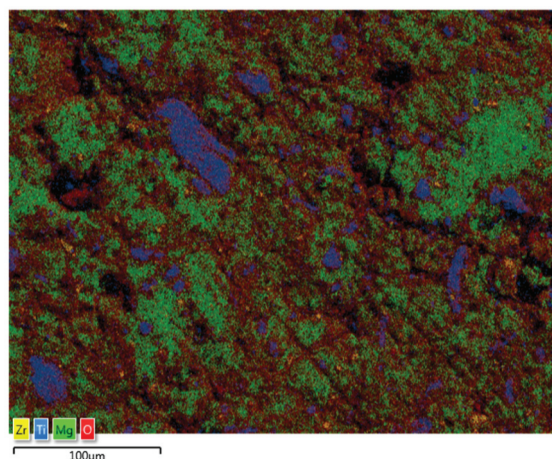
**Figure 2** Structure a-sample, broken surface. Bright particles - Zr, gray particles - Ti.

## 2.1. Structure of composite

The structure of fresh ball-milled (referred to as *b-sample*) and aged composite (*a-sample*) at room temperature in a well-defined atmosphere of dry air for 7 months is showed in **Figures 1, 2**. It was found that the surface of b-sample was “clean”, but surface of Mg grains and others particles of a-sample were covered by oxide layer (**Figures 2, 3 and 4**).



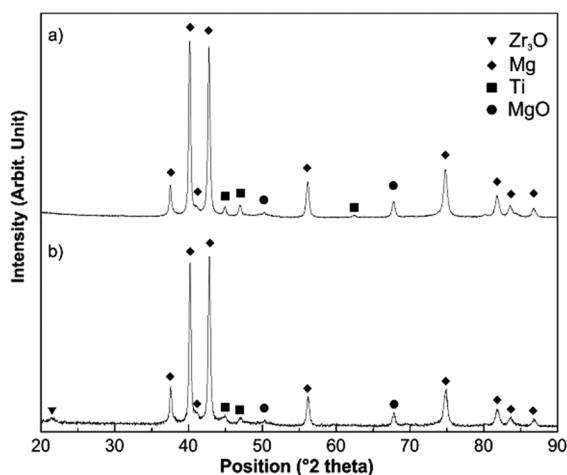
**Figure 3** The EDS map of elements on the slightly grinded surface of the a-sample



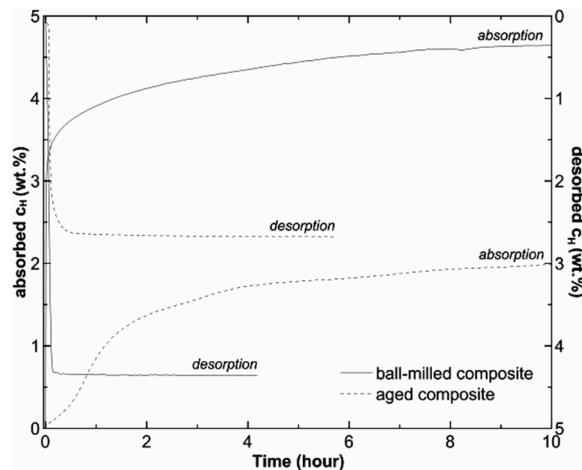
**Figure 4** The EDS map of elements on the surface of the hydrogenated a-sample

The oxidation layer is very well visible in EDS maps of elements of non-hydrogenated and hydrogenated a-sample. Because the surface of aged material was covered by oxide layer (red colour in **Figures 3 and 4**), it was slightly grinded for highlighting the particles of catalysts and also oxide layer for EDS mapping of elements. The b and a-sample contents particles of catalysts Ti (gray, blue) or Zr (bright, yellow) located mainly on Mg (green) grains. The size of Ti, Zr particles varied approximately from 1 to 60 μm and from 1 to 10 μm respectively. The grain size of Mg varied approximately from 10 μm to 100 μm.

The main phases of these samples are shown in XRD patterns (**Figure 5**). The both samples contain mainly phases Mg, Ti and MgO and the a-sample contains also Zr<sub>3</sub>O. The peaks of MgO are very similar in both cases because the thin layer of the MgO in a-sample is under resolution of XRD device. Also the peaks of small particles Zr are not significant in these patterns, because they are superimposed by peaks of others phases.



**Figure 5** XRD pattern of b and a-sample



**Figure 6** Comparison of hydrogen sorption curves of b and a-sample (solid line and dashed line)

The content of oxide phases calculated by Rietveld analysis of X-ray diffraction peaks for both samples is very similar. The content of MgO varied from 2 wt.% to 2.3 wt.% and content of Zr<sub>3</sub>O varied from 0 to 1.3 wt.% for a and b samples respectively. The oxidation is not in the bulk but only on the surface as is better visible by EDS analysis.

The main difference between these samples is that the surface of a-sample has higher degree of oxidation than b-sample. The thin oxidation layer of MgO covered Mg grains and others particles and also filled the spaces between them in a-sample (**Figure 4**).

### 3. RESULTS AND DISCUSSION

The measurements of kinetic curves were done at temperature 623 °C with a starting pressure of 2.7 MPa (for absorption) and 0.1 Pa (for desorption). The instantaneous hydrogen pressure  $p$  in the sample chamber was always sufficiently above the equilibrium pressure  $p_{eq}(T)$  of the respective hydrides and below the  $p_{eq}(T)$  during absorption and desorption, respectively. It is obvious that the a-sample has sufficiently worse sorption properties than b-sample (**Figure 6**). The hydrogen capacity after the ageing was decreased by 45 %.

The XRD analyse did not show significant differences in phase composition of b or a-sample, except of higher content of Zr<sub>3</sub>O in a-sample. However, EDS analysis showed oxidization of surface of Mg and also particles Ti and Zr in a-sample. The surfaces of these phases were covered by thin oxide layer. This oxidation layer is most likely the main reason of degradation of hydrogen storage properties, because it can limit hydrogen diffusion into composite or formation of Mg-hydrides. It also decreases catalytic effect of Ti and Zr particles.

It can be assumed that these particles can provide the pathways for the hydrogen diffusion into the sample, similarly as it was shown in MgH<sub>2</sub>-10 wt.% TiC composite [3]. However one can expected - if these particles and Mg grains are covered by oxide layer - that their catalytic effect can be lower and they also cannot serve as affective pathways for hydrogen in to the composite. Moreover, also the spaces or gaps between of Mg grains in a-sample are filled by this layer and make this material more compact than b-sample. It is means, that a-sample should have less free-surface of Mg grains than b-sample which resulted in slower formation of hydrides.

### 4. CONCLUSION

- 1) In the present work, the ageing process in Mg-1.8Ti-1.9Zr-0.2C composite was investigated. The process was characterized by degradation of hydrogen sorption properties and surface oxidation of grains or particles. The hydrogen storage capacity decreased from 4.7 wt.% H<sub>2</sub> to 2.1 wt.% H<sub>2</sub> at 623 K.
- 2) The degradation of these properties can be caused by following reasons:
  - The surface oxide layer reduces diffusion rate of hydrogen into Mg particles.
  - The oxidation decreased catalytic effect of Ti and Zr particles.
  - Particles covered by oxide layer cannot act as “pathways” for hydrogen into composite.
  - Oxidation also decreases free-surfaces of Mg grains and prevent the formation of hydrides.
- 3) The oxidation is the main factor which causes significant downgrade hydrogen sorption properties of Mg-1.8Ti-1.9Zr-0.2C composite.

### ACKNOWLEDGEMENTS

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