HYDROGENATION PROPERTIES OF MG-AL-TI-ZR-C COMPOSITE

KRÁL Lubomír[1], ČERMÁK Jiří[1,2], ROUPCOVÁ Pavla [1,3]

[1] *Institute of Physics of Materials ASCR v.v.i., Brno, Czech Republic, EU*
[2] *CEITEC - Central European Institute of Technology, Brno, Czech Republic, EU*
[3] *BUT - Brno University of Technology, FME, IMSE, Brno, Czech Republic, EU*

Abstract

The improvement of hydrogen storage properties of ball-milled Mg-Al-Ti-Zr-C composite was studied in this paper. It has been previously shown, that the addition of Ti, Zr, Al and C improves storage properties of Mg. This beneficial effect of additives upon hydrogen storage properties can be explained by catalysis by the nanoparticles rich in Ti, Zr or Al located on the surface of Mg grains. They provide effective pathways for the hydrogen diffusion into the MgH_2. The morphological and microstructural characteristics were investigated by scanning electron microscope Tescan Lyra 3 and by X-ray diffraction. The hydrogen sorption was measured by Sieverts method using Setaram PCT-Pro device.

Studied experimental composite absorbed 4.2 wt.% H_2 at 573 K and 3 wt.% H_2 at 523K within 10 min. The hydrogen storage capacity of the composite was about 4.6% wt.% H_2 and 4.2% wt.% H_2 at 573K and 523K, respectively.

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

1. INTRODUCTION

Hydrogen is very perspective fuel for vehicles which can bring economical and environmental benefits. However, a main obstacle that impedes expected future hydrogen economy is the lack of safe, efficient and economical on-board hydrogen storage. Magnesium is considered as a promising candidate for hydrogen storage due to its high theoretical hydrogen storage capacity (7.6 wt%), high volumetric capacity (110 g L^{-1}), highest known energy density of all reversible hydrides (9 MJ kg^{-1} Mg), good reversibility, earth abundance and low cost [1]. But the kinetics of hydrogen absorption/desorption (A/D) is very poor.

In the past decade, the rapid development of nano-engineering brought the new hope for these metal (complex) hydrides as the new generation of solid-state hydrogen storage materials. Research on nanostrctured hydrogen storage materials has clearly demonstrated that reduced size, low dimensionality and low coordination can significantly lead to very different properties from the bulk counterparts, which were summarized in recent review articles [4], [5], [2], [3], [6] and [7]. Tremendous efforts have been devoted to address these issues by taking advantage of nano-size and catalytic effects, including the use of chemical modification via catalysts/additives doping, Mg crystals nanostructuring and nanoconfinement in porous scaffolds.In recent times, the size and catalytic effects was the one of most frequent ways for improvement of hydrogen storage properties. The origin of these effects can have mainly two reasons when particles sizes are at nanoscale: (i) an increase of surface energy when the particles get very small; and (ii) lower atom coordination and unsatisfied bonds appear.

The nanolayered Mg-Ti based materials show greatly improved sorption properties. The strong catalytic effect of nanolayers of Ti/Pd or Al was found in new nanolayer material Ti/Mg/Ti/Pd and Mg-AlTi. [8, 9, 10]The multilayered Mg-AlTi material (34 nm Mg and 2nm AlTi) showed good hydrogen A/D cycles stability with remarkable kinetics [10]. The addition of TiC nanoparticle led to a pronounced improvement in the de/hydrogenation kinetics of MgH_2 in MgH_2-10 wt.% TiC. The improved hydrogen storage properties were ascribed to the TiC particles embedded in the MgH_2, which provided the pathways for the hydrogen diffusion into this composite [11]. But for good catalytic effect of catalysts and hydrogen storage properties of these materials is crucial issue how to suppress the oxidation [16]. However, catalyst based on Ti is also useful in other promising hydrogen storage materials. For example, homogenously dispersed TiC nanoparticles act as a surface catalyst on the Li-alanate and also improves hydrogen sorption properties [12].

Other very effective catalyst added to Mg-based materials is carbon, including graphite, activated carbon, carbon black, fullerene and single-walled carbon nanotubes (SWCNT) [13]. In paper [14], 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 $c_C \cong 5$ 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.

In this paper, sorption properties in experimental ball-milled composite of Mg which contents Ti, Zr, Al and C as catalysts were studied.

2. EXPERIMENTAL

The experimental composite Mg-11Al-10Ti0.5ZrC (wt.%) was ball-milled from pure components (splinters of 3N8 Mg, 3N6 Ti, 5N Zr, 5N Al and spectroscopic pure C powder) using the ball-mill Fritsch-Pulverisette6 under hydrogen atmosphere in two steps. The first of all, the components Ti-1Zr-1C (wt.%) were milled (400 rpm, 30 min milling / 15 min cooling - repeated 24 times). After that, components Mg-10Al - 10(Ti-1Zr-1C powder) (wt.%) were milled together (400 rpm, 20 min milling / 40 min cooling - repeated 24 times). The coarse parts of final powder were separated by use the 450 µm sieve. This powder Mg-11Al-10Ti-0.5Zr-C (wt.%) was compacted at room temperature into pellets with diameter 20 mm × 2 mm in height.

The observation of structure and 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. This equipment enables safe and fully-automated repeated measurements in both absorption and desorption regimes. The measurements of kinetic curves were done at temperatures 573 and 523 K with a starting pressure of 3 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. 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 $CuK\alpha_{1,2}$ radiation. HighScore Plus software HighScore Plus software and JCPDS PDF-4 was used for qualitative analysis and Rietveld refinements using external LaB_6 standard and structural models based on the ICSD database for quantitative analysis.

3. RESULTS AND DISCUSSION

The Mg powder of composite contained very fine bright submicron and nanometer particles (**Figure 1**). The particles content mainly Ti and Al and some of them also higher content of Mg, Zr seems to be spread quite homogenously or it correlates with nanoparticles (**Figure 2**).

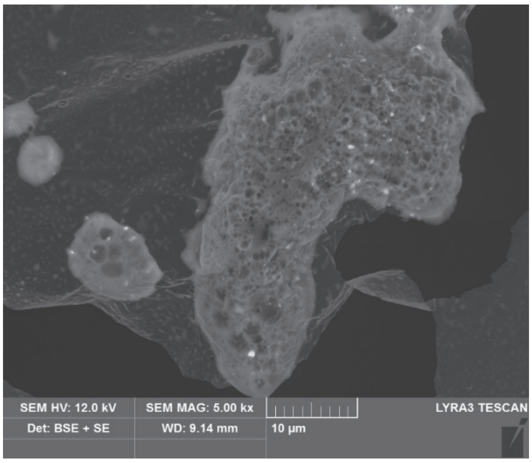

Figure 1 The Mg grains of powder placed on graphite foil, hydrogenated state

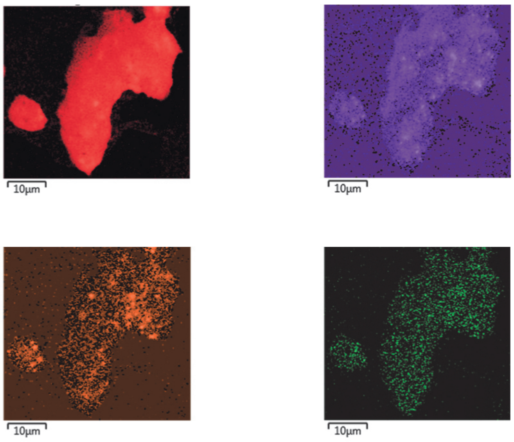

Figure 2 The EDS map of Mg grains (**Figure 1**), Mg (red), Al (purple), Ti (orange), Zr (green)

The main phases of this ball-milled and hydrogenated composite are shown in XRD spectra (**Figure 3**). Ball-milled material consists about seven phases, but after hydrogenation it consists about five phases only. The main phase for hydrogen storage is MgH_2, and Ti or Al type particles can be considered as catalysts. The peaks of small phases containing Zr (**Figure 2**) are not significant in these spectra, because they are superimposed by peaks of others phases. This material does not content MgO and oxidation was very low. We can expect that the preparation of this material under hydrogen atmosphere is sufficient for avoiding of oxidation.

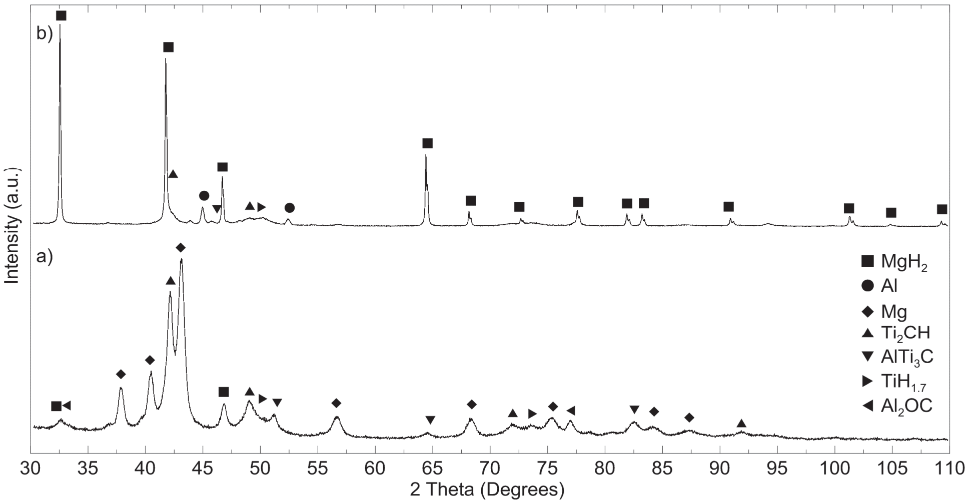

Figure 3 XRD spectra of experimental material, a) ball-milled b) hydrogenated at 523K

The measurements of kinetics curves were done after two A/D cycles at 623K/2 hours. This initial step is important for reach stable structure of composite. The kinetic curves of composite and material Mg+10TiZrC [16] are shown in **Figure 4** and **5**. There is significant difference in kinetics of sorption at experimental temperatures, but the maximum hydrogen capacity of composite is quite similar.

In comparison to similar powder materials published in literature [16, 17], the sorption properties of experimental composite were enhanced. The experimental composite show better kinetics and higher hydrogen capacity (4.6 wt.% H_2) at temperature 573K than material Mg+10TiZrC (4.7 wt.% H_2) [16] and nanomaterial Mg-10Ti (3.63 wt.% H_2) [17] at temperature 623K.

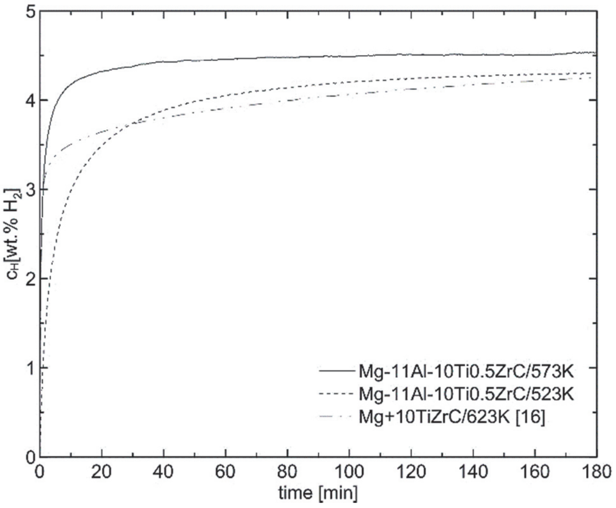

Figure 4 Hydrogen absorption curves of experimental composite and Mg+10TiZrC [16]

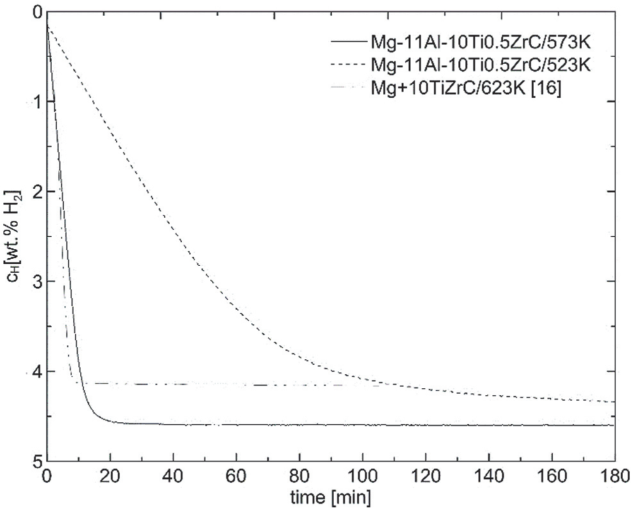

Figure 5 Hydrogen desorption curves of experimental composite and Mg+10TiZrC [16]

It seems to be very crucial, that both of these materials contain MgO in contrast to experimental composite. It was shown in our previous work [16] that oxidation significantly decreased hydrogen sorption properties of Mg-Ti materials. However, the studied composite contained oxide phase Al_2OC only after ball-milling but this phase and also $AlTi_3C$ decompose during initial cycles of hydrogen sorption. The hydrogenated composite contain only Al phase. It seems that addition of aluminum and carbon into this type of materials together with ball milling of splinters under hydrogen atmosphere very effectively suppresses the oxidation.

The addition of zirconium, aluminum and carbon into the Mg-Ti composite significantly improve hydrogen sorption properties. Aluminum and carbon seems to be very strong antioxidant components in this composite. We can expect that the surfaces of Mg and other catalysts are oxide free in this study composite. It is means, that diffusion of H into Mg and catalyst effect is not limited by oxidation. This is probably one of main reason why this composite has better sorption properties than composites published in papers [16, 17].

4. CONCLUSION

1) In the present work, the composite Mg-11Al-10Ti0.5ZrC (wt.%) was studied. The addition of Al, Ti, Zr and C significantly improve hydrogen sorption properties compared with sorption properties of Mg-Ti composites published in literature. The hydrogen storage capacity was 4.6% wt.% H_2 and 4.2% wt.% H_2 at 573K and 523K.
2) Addition of aluminum, carbon in the Ti composite and ball-milling under hydrogen atmosphere improves oxidation resistance of the composite. The low level of oxidation protects before:
   - Reduction of diffusion rate of hydrogen into Mg particles. It keeps the free-surfaces of Mg grains “clean”.
   - Decreasing the catalytic effect of Ti and Zr particles. Particle act as “pathways” for hydrogen into composite.

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