



Hydrogen storage properties of bulk nanostructured ZK60 Mg alloy processed by Equal Channel Angular Pressing

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ABSTRACT

It is shown that hydrogen storage materials nanostructured by Severe Plastic Deformation (SPD) retaining the bulk shape are capable to meet or even exceed the adsorption/desorption kinetics of their ball milled counterpart. The grain size of commercial magnesium alloy ZK60 was decreased by Equal Channel Angular Pressing (ECAP) down to 250 nm – the smallest value ever achieved by this technique. The material exhibits high gravimetric hydrogen storage capacity of 6.6 wt.% and rapid hydrogen desorption kinetics of less than 5 min at 350 °C. Furthermore, the influence of grain size, surface oxidation and of the addition of metallic chromium as catalyst on the storage capacity and kinetics was investigated. A new method for rapid activation in only one charging/discharging process was successfully tested. The long-term durability of the material was proven in a cyclic sorption/desorption test up to 1000 cycles; no deterioration in storage capacity or in kinetics was observed which is exceptional for nanomaterials for hydrogen storage. Finally, the pressure–composition isotherms of ZK60 were extended by new plateaus at low temperatures (200–260 °C).

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1. Introduction

Compared to hydrogen stored in its liquid or gaseous state, reversible solid state light-metal hydrides offer considerable advantages, such as high volumetric and high gravimetric storage capacities [1]. Concerning Mg, it has the highest storage capacity of all metal hydrides (7.66 wt.% hydrogen), it is light, abundant, low-priced, environmentally benign (non-toxic and reusable) and can be produced in large quantities [2,3]. However, due to the rather sluggish absorption and desorption kinetics, Mg has not been considered competitive in practical applications for a long time. For two decades several efforts have been undertaken to increase especially the storage kinetics. Successful improvements were achieved in the early 1990s by alloying pure Mg with metallic catalysts such as Ni, Ti, Fe, Pd, V and Mn [4,5]. Later, a substantial breakthrough was the refinement of the microstructure down to nanosized grains by means of High-Energy Ball Milling (HEBM) [6,7]. The massive introduction of lattice defects, namely grain boundaries tremendously increases the diffusion of hydrogen which migrates along

those boundaries. Thus the charging and discharging times of nanocrystalline magnesium powder could be radically reduced to few minutes by reducing the grain size down to some tens of nanometres. In the next step the hydrogenation kinetics of Mg hydride was further enhanced by the combination of nanostructuring by HEBM with the addition of small amounts (e.g. 0.2 mole%) of non-metallic catalysts [8,9]. These additives, mainly oxides, are supposed to catalyze the dissociation of H₂ molecules on the metal surface and to lower the strength of the Mg–H bond.

Although an enormous acceleration of hydrogen sorption and desorption could be achieved by HEBM the technique exhibits several intrinsic disadvantages: it is time- and energy-consuming, thus expensive, and it needs extensive precautions to keep the material pure and dense, and to minimize the environmental, fire and health risks.

All those disadvantages can be avoided when bulk, nanostructured Mg alloys as hydrogen storage materials are processed by methods of Severe Plastic Deformation (SPD). Starting from a conventional, coarse-grained structure these methods can produce clean, fully dense, bulk ultrafine-grained rods of metals and alloys. The most common SPD method is the ECAP technique which consists, in principle, in multiple pressing of a billet through a die made up of two equal channels with a defined angle of intersection, commonly 90° or 120°, under enhanced hydrostatic pressure without changing the original shape of the samples. The latter feature enables very high deformation by repeated pressing using various

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deformation paths, which, together with the number of passes and the temperature, has a strong effect on the final microstructure obtained. The details of ECAP are described elsewhere [10]. Due to comparably short processing times (minutes), handling under air and relatively simple set-ups (including those for continuous ECAP processing [10,11]) there is a high potential in saving of production costs compared to HEBM.

In 2004, in a pioneering work, Skripnyuk et al. [12] showed that the hydrogenation properties of the commercial Mg alloy ZK60 processed by means of (ECAP) are similar to those of the ball milled one. This was confirmed by later publications [13,14] and very recently by Wang et al. [15]. The mechanical properties of the ZK60 alloys were also subject of investigations [16,17].

The present work focused on the following tasks: (i) the impact of nanostructuring of the Mg alloy ZK60 by means of ECAP on the thermodynamics and kinetics of the interaction with hydrogen, (ii) the effect of alloying with chromium as catalyst, (iii) investigation of oxidation during sample preparation and handling under air, (iv) rapid activation of Mg filings in one single sorption/desorption process, (v) the proof of the long-term stability of the ECAP-processed ZK60 alloy up to 1000 sorption/desorption cycles and (vi) determination of new, low-temperature pressure–composition isotherms of the ZK60–H system.

2. Experimental

2.1. Materials

Three kinds of materials were investigated in the present study: (i) a commonly used, commercially available structural magnesium alloy ZK60, (ii) the same ZK60 alloy with a small amount of chromium as catalyst and (iii) Mechanomade® P930, a commercially available, nanostructured Mg-based hydrogen storage material for reference (Table 1). ZK60 of composition: 5 wt.% Zn; 0.8 wt.% Zr; Mg balance, as well as ZK60 with nominal 1 wt.% Cr were cast by LKR Leichtmetallkompetenzzentrum Ranshofen GmbH, Austria. Mechanomade® P930 is a commercial, Mg-based hydrogen storage material with catalysts Co, Ni, Cr, V, Cu, Fe, Mn, Mo, Al, C, Si, Ti, W, manufactured by HEBM and supplied by MBN Nanomaterialia S.p.A., Italy. Its particle size was between 38 and 500 µm and its grain size was 19 nm; the skeletal density amounted to 2.14 g/cm³. Mechanomade® has a gravimetric storage capacity of >5.6 wt.% hydrogen, a volumetric capacity of 0.12 kg hydrogen per litre and can be fully charged within 13.3 min.

2.2. Microstructure refinement by Equal Channel Angular Pressing (ECAP)

The microstructure of as-cast (ZK60–Cr) and extruded alloys (ZK60) was refined by ECAP at AIT Austrian Institute of Technology GmbH, Seibersdorf, Austria. Samples in shape of cylindrical bolts with 20 mm in diameter and 90 mm length were heated up directly in the ECAP tool and then pressed under air though an ECAP die with internal channel angle of intersection $\Phi = 120^\circ$, the angle of curvature at the point of intersection (the outer arc of curvature) $\Psi = 60^\circ$, at constant ram speed of 5 mm/s, without back pressure, using a graphite lubricant and route B_c (for definitions of various pressing routes see e.g. [10]). The accumulated strain for one pass ε_{ECAP} was approximately equal to 0.6 [10]. ZK60–Cr was pressed four times at constant temperature of 200 °C, whereas in case of ZK60–10x the processing temperature was gradually lowered from initially 200 °C down to 110 °C in 10 °C steps resulting in altogether 10 passes. Further, in an attempt to reduce the number of ECAP passes and thus the potential production costs of ZK60 for commercial applications ZK60–4x was pressed only four times: two times at 300 °C, then at 235 °C and finally at room temperature. Additionally to ECAP and in order to estimate the minimum grain size that can be achieved by an SPD method, two samples of ZK60 (diameter 10 mm, sample thickness 1.08 mm) were heavily deformed by High Pressure Torsion (HPT) at RT under a hydrostatic pressure of 2 GPa by four rotations (true equivalent strain of 134) at 0.2 rpm.

2.3. Microstructural investigations, mechanical properties

The microstructure of the magnesium alloys was investigated by Optical Microscopy (OM) using a Zeiss optical microscope Axioplan MC 80 with computerized imaging system and evaluation software. Electron microscopy works were done at a Transmission Electron Microscope (TEM) Philips CM200 and a Scanning Electron Microscopy (SEM) Phenom of the FEI Company. The mean grain size was calculated using the 'analySIS work' software package by Olympus Soft Imaging Solutions GmbH. Additionally, measurements of Vickers micro- and macrohardness (HV10) of the ZK60 alloys were carried out with a microhardness tester of type MHT-4 (Anton Paar GmbH, Graz, Austria) equipped with a diamond Vickers inden-

ter attached to the optical microscope described above (load 0.5 N, indentation time 10 s), and a macrohardness tester of type HT2a Otto Dohmen & Co., respectively.

2.4. Charging and discharging with hydrogen

Hydrogenation experiments were carried out in a newly designed, portable, hydrogen charging Sieverts' apparatus [18]. After removing the outer layer from the surface of the ECAPed bolts the materials were comminuted to filings in the range of 0.5–1 mm either under air, under low-purity Ar or under highest-purity protective atmosphere (Ar) in a glovebox (Jacomex GP T4-CA) with gas purification system. With the filing, some plastic deformation occurred which, however, can be neglected at least in case of the samples processed by ECAP [13]. After filing, samples were weighed by a high accuracy microgram balance Sartorius M3P and charged at constant temperatures between 350 °C and 200 °C with hydrogen of 5.0 purity (99.999%). During charging and discharging the pressure of gaseous hydrogen was held between two set threshold values around 1.5 MPa and 0–0.1 MPa, respectively. The process was fully controlled by a computer system that also acquired the data. The exact hydrogen uptake was calculated from changes in the gas pressure and from known, well calibrated volumes of the apparatus using the standard ideal gas equation. The samples were placed in a sample chamber with internal volume of $50 \pm 1 \text{ cm}^3$, made of stainless steel and directly heated by a built-in resistance heating. The temperature was controlled within an accuracy of $\pm 1 \text{ K}$ and additionally measured directly on the sample by an embedded thermocouple of type K.

3. Results and discussion

3.1. Microstructure after ECAP

The main aim of applying ECAP was to minimize the grain size in a minimum number of passes. The results of the mean grain size as well as micro- and macrohardness are listed in Table 1. It is clear that the lower the (final) processing temperature the smaller has been the grain size [19]. Note that just four ECAP passes performed at appropriate conditions can produce ZK60 with 250 nm grain size which is the lowest value ever achieved in Mg alloys by ECAP and only insignificantly larger than after extremely large plastic deformation by HPT at RT (200 nm).

Up to now a final average grain size of only 0.8 µm [13,17,20,21], 1.4 µm [16] and 1.0–1.8 µm [22] was reported after ECAP under different conditions (temperature, interior die geometry: Φ , Ψ , processing route). Comparable grain refinement down to sub-micrometer size of 0.5–1 µm was observed in other magnesium alloys processed by ECAP [23,24].

The key for achieving such a small grain size lies in solving the problem of poor formability of the hcp matrix of ZK60 at temperatures below the brittle–ductile transition. Here the number of slip systems is quite limited resulting in material failure and crack formation. In this situation, however, the workability of Mg alloys can be enhanced by ECAP processing at high temperatures (250–350 °C for ZK60) and leaving the final passes to be done at temperatures below this limit. Thus, by gradually lowering the processing temperature of ZK60–10x and ZK60–4x down to 110 °C and even RT, we were able to reduce the grain size to 300 nm and 250 nm, respectively. Very recently the same method has been applied to pure Mg with the final pressing at RT, too, resulting in a grain size of ~250 nm [19]. The finer structure was achieved in ZK60–4x despite the smaller deformation (accumulated strain $\varepsilon = 2.4$) than in the case of ZK60–10x ($\varepsilon \approx 6$), and it is very close to the value of 200 nm obtained by HPT deformation at room temperature to the equivalent strain $\varepsilon_{HPT} = 134$ (Table 1).

A detailed discussion of the mechanical properties of ECAP and HPT deformed ZK60 is beyond the scope of this paper and will be addressed elsewhere.

3.2. Hydrogen properties

3.2.1. Kinetics vs. temperature

Representative sorption kinetics vs. temperature obtained on ZK60–10x prepared under low purity Ar and after three full cycles at 350 °C for activation is shown in Fig. 1 (for more results s. [25]).

Table 1
Materials investigated, equivalent deformation strain, mean grain size and hardness.

Sample label	Material	Processing path and temperature (°C)	True equi-valent strain ϵ	Grain size (nm)	Vickers microhardness (GPa)	Vickers macrohardness (HV10)
ZK60-0	ZK60	Extrusion	?	2600	0.61	53.4
ZK60-10x	ZK60	Extrusion, ECAP 10xBc, 200–110	6.05	300	1.00	–
ZK60-4x	ZK60	Extrusion, ECAP 4xBc, 200–RT	2.42	250	–	–
ZK60-Cr	ZK60 + Cr	Casting, ECAP 4xBc, 200	2.42	560	0.95	0.95
ZK60-HPT	ZK60	HPT 4 rotations, RT	134	200	–	–
Mg-HEBM	Mg + catalysts	HEBM	–	19	–	–

It can be seen that below 300 °C the kinetics strongly depends on temperature. The slightly higher kinetics measured at 300 °C and the 7th cycle compared to 350 °C and the 4th cycle indicates that the activation process was not completed at this time; this has been later confirmed by the cyclic tests (see Section 3.2.6). In contrast, the storage capacity is not temperature-sensitive, however, at lower temperatures it takes days to reach the fully charged state (not shown in Fig. 1). Furthermore, the curves exhibit two stages: first, rapid hydrogenation of the outer layer of the particles with a mean rate of 0.3 wt.% hydrogen per min up to 3.5 wt.% in only 10 min; after 20 min the process decelerates to 0.0043 wt.% hydrogen per min or 0.26 wt.% H/h because further charging is controlled by the slow process of hydrogen diffusion through the hydride layer into the interior of bigger particles (see Section 3.2.2).

Considering the first 40 min of charging the fastest sorption kinetics at 300 °C was that of the ZK60-4x sample, being 0.12 wt.% H/min (or 7 wt.% H/h). The reason for that lies on the one hand in the smallest grain size of only 250 nm, on the other hand in preparation under protective atmosphere. During rapid charging the sample temperature rose temporarily up to 388 °C. For comparison with the ECAP processed samples Fig. 1 also shows the sorption kinetics of Mechanomade® P930 HEBM powder which admittedly exhibits a far higher charging rate of almost 1 wt.% H/min, due to both effects, i.e. the small grain size and the catalyst content.

The kinetics of hydrogen desorption at 300 °C from ZK60 processed by four ECAP passes resulting in 250 nm grain size and handled under high-purity Ar is shown in Fig. 2. It takes only about 12 min to desorb 6.6 wt.% of hydrogen. For comparison results obtained on the Mechanomade® P930 at the same conditions as well as data on ECAP and/or HEBM processed ZK60 published in [12] are presented. Desorption in ZK60 is particularly fast in the time range between 4 and 7 min where the desorption rate reaches about 1 wt.% H/min, corresponding to 120 MJ/min or 2 MW or 2680 hp per

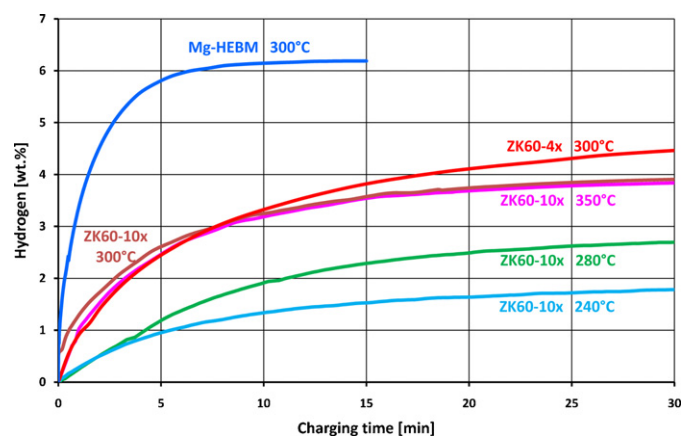


Fig. 1. Sorption kinetics vs. temperature of ZK60-10x prepared under low purity Ar and of ZK60-4x and of a HEBM Mg powder Mechanomade® P930 with catalysts, both handled under high-purity atmosphere. The latter two have the fastest sorption kinetics because of small size of grains, and because of the presence of catalysts, respectively.

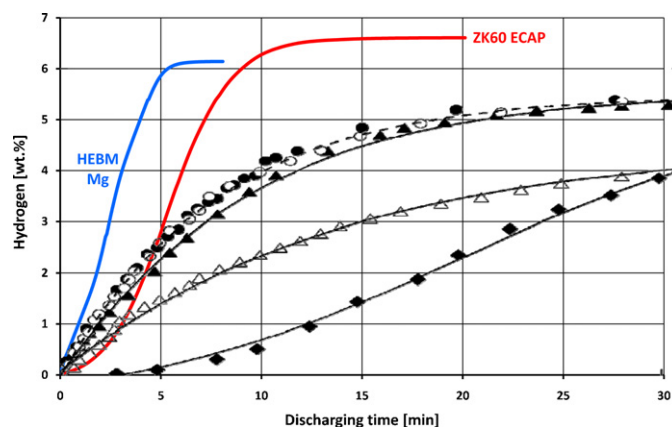


Fig. 2. Comparison of hydrogen desorption kinetics at 300 °C of differently processed nanostructured materials from ZK 60 alloy and pure Mg without and with catalysts: ZK60-4x processed by 4 ECAP passes reaching 250 nm grain size, and handled under high-purity Ar (red line, this work); ZK60 alloy fabricated by HEBM and/or ECAP (from [12]): ●, ZK60 ECAP and HEBM-processed; ○, ZK 60 after ECAP; ▲, ZK60 after HEBM; ◆, ball milled pure Mg; △, coarse grained ZK60 alloy); HEBM Mg powder with catalysts (Mechanomade® P930, blue line, this work). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

100 kg storage material. It is to be emphasized that in desorption – in contrast to the case of sorption – the kinetics of commercial catalytic Mg powder Mechanomade® P930 with much smaller grain size is only insignificantly faster. Due to the high desorption kinetics and low thermal conductivity of the powder the temperature on the sample fell down to 280 °C.

3.2.2. The effect of grain size on the hydrogenation rate

The effect of the grain size in bulk ECAP processed ZK60 on the hydrogen sorption kinetics is shown in Fig. 3. By reducing the grain size from 2600 nm down to 300 nm the kinetics gets almost twice as fast. Diffusion along grain boundaries is much faster

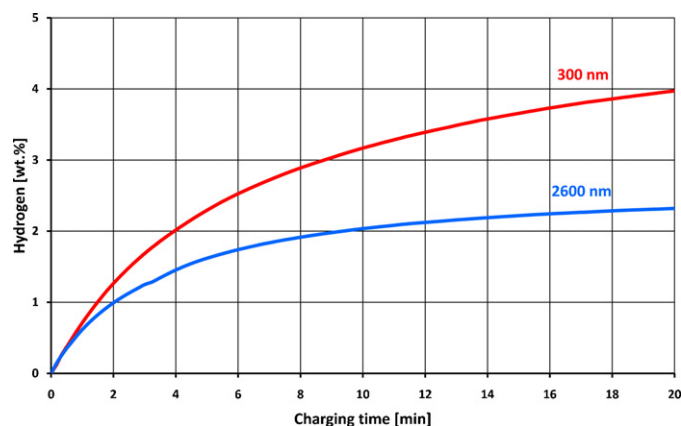


Fig. 3. Grain-size effect on the sorption kinetics at 350 °C in extruded and ECAP-processed ZK60-10x prepared under air.

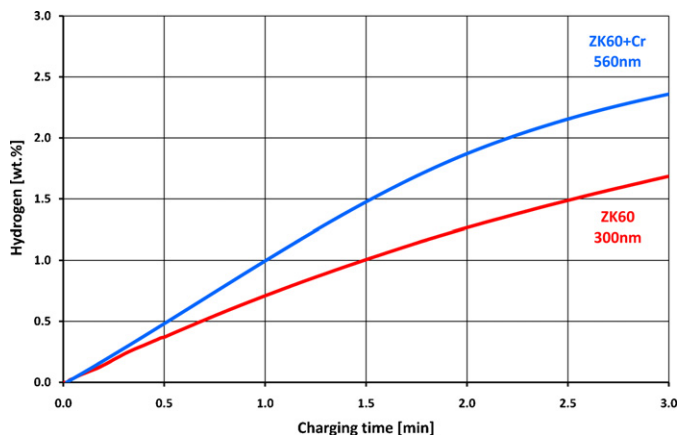


Fig. 4. Effect of metallic chromium as catalyst on desorption kinetics at 350 °C: ECAP-processed ZK60-10x (300 nm, red line) and ZK60-Cr (560 nm, blue line); both samples prepared under low-purity Ar. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

than in the bulk since the packing density at grain boundaries is lower. Moreover, grain boundaries are favourable nucleation sites for phase transformations (α -phase to β -phase and vice versa). Since the diffusion coefficient at 350 °C in magnesium hydride (β -phase; $D \leq 2.5 \times 10^{-13} \text{ m}^2/\text{s}$ [26]) is three to four orders of magnitude lower than in the solid solution (α -phase; $1.5 \times 10^{-8} \text{ m}^2/\text{s}$ [11] or $1.7 \times 10^{-9} \text{ m}^2/\text{s}$ [27]) it is clear that the hydride layer in the outer part of a particle diminishes drastically the charging kinetics and prevents further charging of the interior of larger particles.

3.2.3. Effect of catalysts

It has been repeatedly reported that the addition of even very low amount of metal oxides (some hundreds mmol.%) to Mg does significantly affect most notably the desorption of hydrogen but also the charging process [8,9,28]. Although the catalytic mechanism is still not entirely clear it is supposed that catalysts promote primarily splitting/recombination of H_2 molecules on the metal surface and so the physical adsorption. However, all reported investigations have been performed on Mg powders produced by HEBM, where Mg can be easily mechanically alloyed with any types of metals, metal oxides or ceramics. For grain refinement through ECAP it was necessary to cast the ZK60 alloy with (a) pure metal(s) whose oxide(s) is/are known as catalysts, and then to expose the material to air in order to oxidize the metallic compound on the surface. Pure chromium was chosen for this purpose as it was reported that the addition of only 0.2 mole% of Cr_2O_3 to HEBM Mg considerably enhances the kinetics of hydrogen desorption [9,28] and that the $\text{MgH}_2\text{-Cr}_2\text{O}_3$ composite possesses satisfactory cycling and thermal stability [28].

After casting a special batch of ZK60 alloy with nominal 1 wt.% Cr the microstructural investigation confirmed the existence of saturated solid solution of Cr in the whole magnesium matrix and revealed that the excess Cr solidified as Cr and ZrCr_2 precipitates. The effect of Cr on kinetics is demonstrated in Fig. 4. ZK60 alloyed with minor content of Cr exhibits better kinetics than the same material without Cr, despite the significantly larger grain size of the alloyed material. This has been the first example of a catalytic enhancement of H_2 storage kinetics in an SPD processed material.

3.2.4. Effect of the oxidation on the kinetics and storage capacity

The massive bolts of ECAP material had to be reduced to smaller pieces in order to increase the surface and thus to allow hydrogen to penetrate the whole material volume in a reasonable time. However, Mg reacts easily with oxygen and air humidity. Conse-

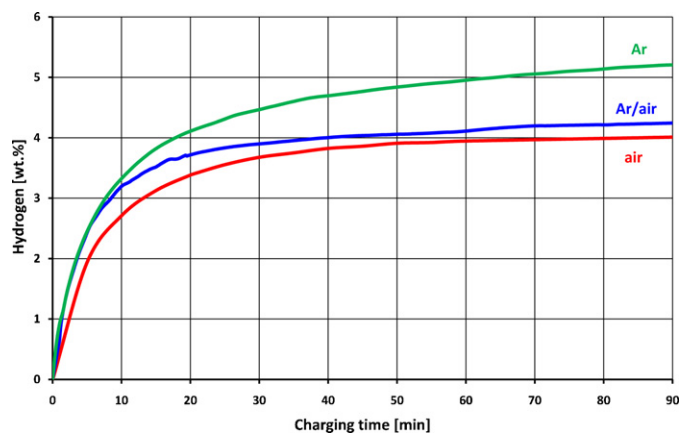


Fig. 5. Influence of handling atmosphere on the charging kinetics at 300 °C and storage capacity of ECAP ZK60.

quently after exposure to air the surface is covered with a layer of magnesium oxide/hydroxide that hampers the dissociation of molecular hydrogen as well as the diffusion of hydrogen atoms into the particles. As a result, surface penetration becomes the slowest process of the overall kinetic rate. Formation of the oxide/hydroxide layer can be avoided by performing the preparation and handling of the granules under protective atmosphere. However, with regard to mass production, this is an expensive process that should be avoided. Therefore, the effect of surface oxidation during comminution on hydrogen storage capacity and kinetics was investigated. Three samples were prepared under (1) air, (2) low-purity Ar and (3) high-purity Ar protective atmosphere. The total preparation time was 90 min; then the samples were activated and charged with hydrogen. Results of sorption at 300 °C are shown in Fig. 5. For better understanding of the influence of MgO in the sorption performance of the material, X-ray powder diffraction measurements would have been desirable. However, due to high oxygen affinity of Mg and therefore vast technical effort, the measurements have been not carried out yet, albeit they are planned in the near future.

3.2.5. Rapid activation

Almost all data of hydrogenation properties of bulk metal hydrides has been obtained on samples subjected to the so-called surface activation process in which prior to the measurement the samples have been processed by up to five desorption–absorption cycles. During the measurement, the thin and brittle oxide layer on the surface chaps due to the volume misfit between hydride and host metal, and the cracks act as channels for hydrogen to reach the metal surface. With increasing number of cycles both the kinetics and the storage capacity gradually increase (Fig. 6). This activation process is particularly required for metals with high affinity to oxygen, i.e. Mg. On the contrary, no initial activation is needed for HEBM Mg with oxide catalysts [28]. Although the activation is simple from industrial point of view, it is time- and energy-consuming and thus should be avoided. Accordingly, we tried to find a way to activate ZK60 in one cycle only. This was achieved by promoting crack formation by introducing thermal stresses by rapid heating up the material under hydrogen pressure of 15 bars/1.5 MPa up to 350 °C and subsequent cooling down to 70 °C in 30 min by a specially designed water cooling system [18]. Immediately during the next charging (Fig. 6) and discharging the material shows very fast kinetics and the final storage capacity of 6.6 wt.% hydrogen indicated that ZK60 was fully activated. Since the temperature during the 1st charging was not kept constant it is not possible to calculate the amount of absorbed hydrogen precisely.

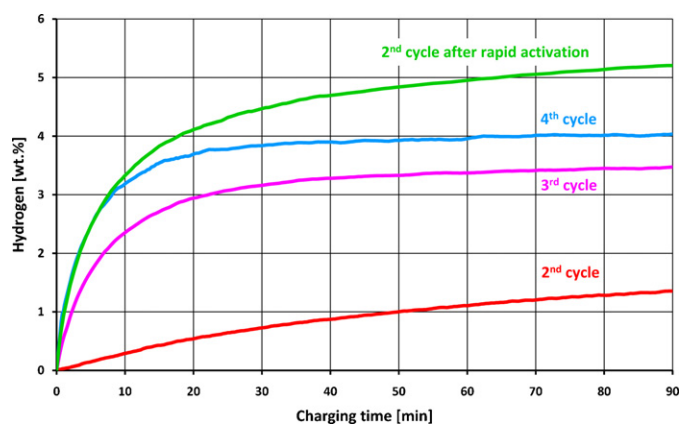


Fig. 6. Comparison of sorption kinetics at 350 °C of ECAP ZK60 (i) conventionally activated by cyclic charging and discharging (2nd, 3rd and 4th cycle, no data for 1st charging available, see text) with first charging process (i.e. 2nd cycle) after rapid activation by introducing thermal stresses.

3.2.6. Long-term cycling stability with regard to storage capacity and kinetics

Some questions regarding durability of the material may arise. During hydrogenation and uptake of hydrogen internal stresses caused by volume expansion as well as by phase misfit can cause changes in the microstructure leading to degradation of the superior properties of ECAP ZK60. Additionally, impurities in gaseous hydrogen can poison the metal surface. On the other hand – during repeated charging/discharging the particle size may further decrease and the kinetics become faster. To answer these questions a long-term test consisting of 1000 charging and discharging steps (corresponding to the number of refuels during the life-time of a passenger car) was performed. However, with the full hydrogenation time of up to 24 h a 1000 cycle test would take not less than 2.8 y. On the other hand, about 5 wt.% or 75% of the full storage capacity (6.6 wt.%) can be reached within 1 h. Additionally the discharging time can be reduced from 15 to only 10 min. Thus, in our tests one cycle lasted about 70 min and the whole test with 1000 cycles took just 1170 h or 44 days. A similar procedure to reduce the testing time was applied in earlier cyclical tests [5].

The results of our cycling tests are depicted in Fig. 7. Over the first 50 cycles the kinetics increases considerably, with the next 200 cycles only slightly, and finally it remains constant. An even larger increase in the discharging kinetics was observed over the first 10 cycles, slowing down during the following 100 cycles, and staying constant afterwards. Also the storage capacity increased in the same manner. This is due to improvement of kinetics and the limitation of charging time.

In contrast with the improving kinetics and high stability of the storage capacity reported here for the ECAP processed Mg alloy ZK60, long-term investigations of HEBM pure and doped Mg show some drawbacks: (i) decrease in storage capacity over the first tens cycles [5] or after just 60 cycles [29,30], (ii) considerable deterioration of the kinetics two [29,30], three [31] or even four [28] times. This was associated with crystallite growth and/or decomposition of metastable phases during cycling.

3.2.7. Microstructure of hydrogenated ZK60

An example of thin, rolled-up filings prepared for hydrogenation test is shown in Fig. 8. The material exhibits a relatively large surface, however, also low skeletal density and thus a comparably low volumetric storage capacity.

The microstructure of ZK60 after 15 and 1000 cycles was investigated by Scanning Electron Microscopy and is shown in Fig. 9. After 15 cycles the shape of the filings can be still recognized (Fig. 9a); at

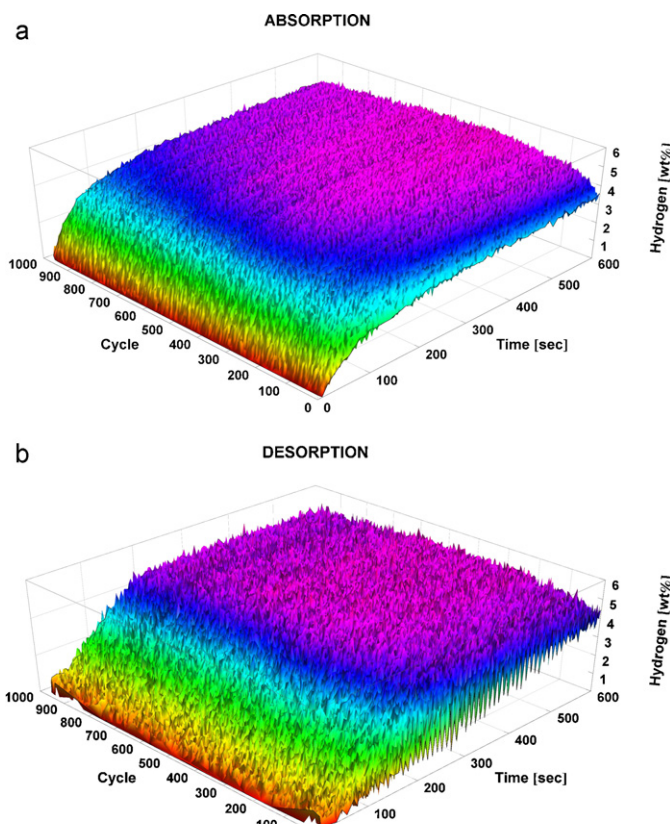


Fig. 7. Colour-coded 3D diagrams showing the storage capacity and kinetics of hydrogen at (a) absorption and (b) desorption of ZK60-4x at 350 °C against cycle number and time.

the same time the material starts to crumble down to particles of about 1 μm size: also first holes are visible. At higher magnification one can see cracks and furrows which constitute paths for molecular hydrogen. After 1000 cycles granules of different particle size (Fig. 9b) appear, similar to those of HEBM Mg. However, the particles are still attached to each other. This fact is advantageous for filtration.

3.2.8. Pressure–Composition–Temperature (PCT) diagram

The Pressure–Composition–Temperature (PCT) diagram of the ZK60 alloy, first published by Skrypnik et al. [12] was extended by four new plateaus at lower temperatures, i.e. 200 °C, 220 °C, 240 °C and 260 °C (Fig. 10). Due to sluggish kinetics at these temperatures and thus long times being necessary to reach thermodynamic

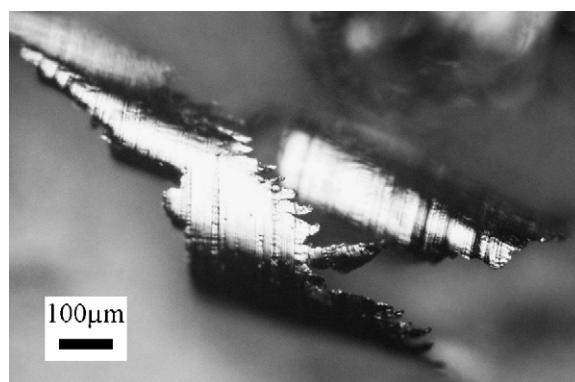


Fig. 8. Optical microscopy image of filings of ZK60 ready for hydrogenation.

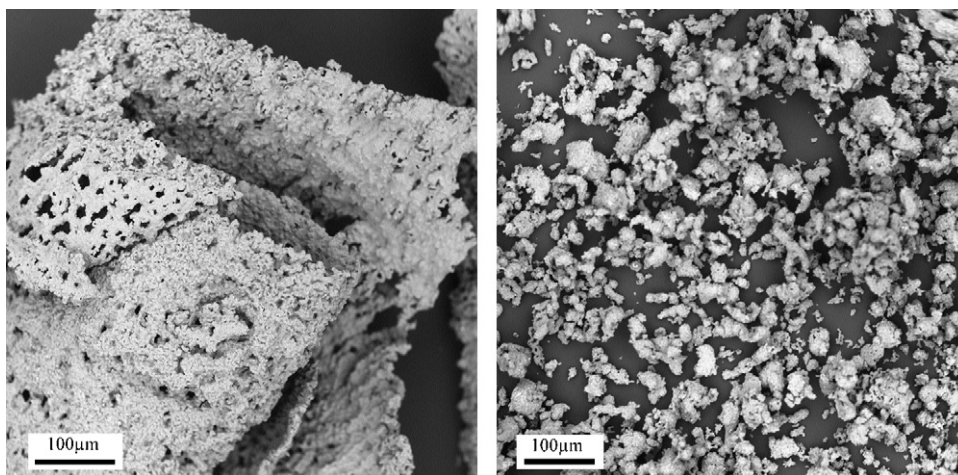


Fig. 9. SEM images of hydrogenated ZK60 after (a) 15 and (b) 1000 charging/discharging cycles.

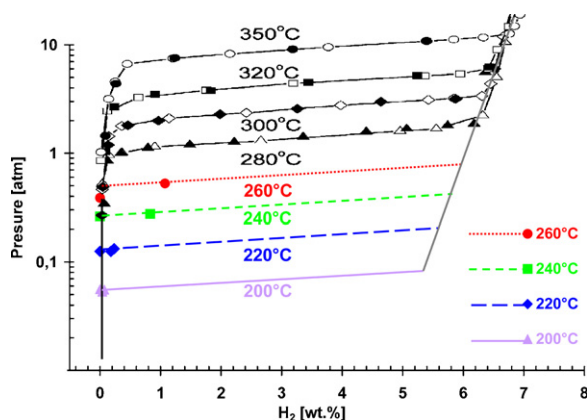


Fig. 10. Pressure–composition isotherms of the ZK60–H system. Coloured data at 200–260 °C on ZK60–4x (this work). Black lines and points determined on ECAP and HEBM processed ZK60 represent the findings of Skripnyuk et al. [12]. Open and filled symbols indicate hydrogen absorption and desorption, respectively.

equilibrium only sorption measurements were performed. They provided single data points on the low-concentration side of the miscibility gap. Nevertheless, these points roughly mark the position of the new plateaus.

The lowest temperature at which the ECAP processed ZK60 could be charged and discharged, the so-called onset temperature, was 200 °C. However, at temperatures below 280 °C the desorption process becomes very sluggish and cannot meet requirements for any practical applications. Thus, because of thermodynamic constraints, the working temperature of the alloy ZK60 remains still higher than 280 °C. Therefore, a hydrogen tank based on ZK60 alloy cannot be solely heated up by the waste heat of proton exchange membrane (PEM) fuel cells, also known as polymer electrolyte fuel cells (PEFC). In consequence, an additional electrical heating is needed dramatically lowering the overall energy performance of the whole system. However, ZK60 can be very well used as hydrogen storage material in combination with a solid oxide fuel cell (SOFC) working at high temperatures, typically between 500 °C and 1000 °C. Further research should focus on particular catalysts to be added to Mg alloys or even on other hydrogen storage materials with lower desorption temperatures, although some concessions regarding the storage capacity may have to be made in both cases.

4. Summary and conclusions

The ECAP technique was successfully applied to extruded ZK60 alloy. The ECAP processed ZK60 has been tested then for its suitability for hydrogen storage. The main results are:

- Grains have been refined down to 250 nm by only four passes, which is the lowest value reported so far being close to 200 nm achieved by room temperature HPT.
- Full hydrogenation of ECAP-processed ZK60 takes 1 day which is rather sluggish compared to only 10 min of HEBM Mg with catalysts. However, 75% of the full storage capacity can be reached within 1 h. On the other hand, hydrogen desorption takes a few minutes being similar to the desorption time of HEBM Mg with much smaller grain size and mixed with catalysts. Thus the dehydrogenation kinetics of ECAP-processed ZK60 appears to be sufficiently fast for mobile applications.
- The activation process of ZK60 alloy can be reduced to only one charging/discharging cycle by rapid heating and cooling under hydrogen pressure.
- ECAP bulk ZK60 alloy can be stored under air. It is conceivable to prepare the final granulate from ECAP ZK60 under air or under poor protective atmosphere in a reasonable time; however, the activation time markedly increases, and storage capacity as well as kinetics suffer considerably.
- The effect of chromium as an additional element to enhance sorption and desorption kinetics was verified in ECAP bulk nano-materials for the first time.
- The long-term cyclic stability being checked in a 1000 cycle test did not exhibit any deterioration in storage capacity or in kinetics.
- Four new plateaus in the PCT diagram of ZK60 were estimated.

To summarize, the ECAP technique proved to be suitable for rapid, low-cost, energy-saving mass production of nanostructured Mg alloys (e.g. ZK60) with desired properties of hydrogen storage avoiding handling of potentially hazardous nanopowders.

Nevertheless, the progress only concerns enhancements of hydrogenation kinetics and does not comprise significant changes of the thermodynamics of the Mg–H system, leaving the reduction of the working temperature as a problem. Therefore, solid state hydrogen storage in bulk magnesium alloys nanostructured by ECAP appears to have its highest potential to be used together with high-temperature fuel cells.

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