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Direct hydriding of $Mg_{87}Al_7Ni_3Mn_3$ by reactive mechanical milling in hydrogen atmosphere and influence of particle size on the dehydriding reaction

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Abstract

Nanocrystalline $Mg_{87}Al_7Ni_3Mn_3$–H was prepared by reactive mechanical milling (RMM) in hydrogen atmosphere. It was found that the amount of the hydride (mainly β-MgH_2) formed during RMM increases in the first 15 h and then reaches an almost constant value of about 34 wt.% (46 vol.%). The thermal stability of the hydride (230 °C) and the enthalpy of H-desorption (55 kJ/mol H_2) determined are lower than those corresponding to conventional polycrystalline MgH_2 as well as to nanocrystalline MgH_2 with different transition metal and transition metal oxide catalysts. The first dehydriding reaction of the $Mg_{87}Al_7Ni_3Mn_3$ hydrides with different particles size was investigated. The finer particle fractions contain essentially a larger amount of MgH_2 than the coarser ones, as the thickness of the hydride layer was estimated to be approximately the same for all particles, about 2 μm. This value was found to be close to the critical thickness of the impermeable hydride layer formed under the experimental conditions of RMM applied in the present study. Isothermal kinetics analysis reveals that the first dehydriding reaction after mechanical grinding in hydrogen atmosphere is surface controlled. In the advanced stage of the dehydriding process diffusion controlled hydrogen desorption was detected. An interface controlled growth model was found to describe some of the kinetics curves, as well. Activation energies of dehydriding of 100–115 kJ/mol were obtained for the nanocrystalline $Mg_{87}Al_7Ni_3Mn_3$–H_x.

Keywords: Magnesium alloy; Reactive mechanical milling; Hydriding; Dehydriding kinetics

1. Introduction

In the last years, Mg and its alloys have attracted huge interest as hydrogen storage materials. The slow H-sorption kinetics of the Mg alloys and the high dissociation temperature of MgH_2, however, limit their practical application. A number of efforts have been made in order to achieve better H-storage performance of Mg alloys, both from the gas-phase [1–3] and electrochemically [4,5]. Bormann et al. [6–9] studied the effect of different catalysts on the hydrogen sorption reaction and showed clearly the high efficiency of transition metal oxides as catalyst for hydrogen sorption of Mg. Excellent H-sorption kinetics of nanocrystalline Mg plus Nb_2O_5 catalyst at temperatures about 100 °C lower than the temperature of dissociation of conventional MgH_2 were obtained.

In our previous studies [10,11] nanocrystalline and nano-/amorphous $Mg_{1.9}M_{0.1}Ni$ (M = Ti, Zr, V) alloys were synthesized by mechanical alloying (MA) and by MA followed by annealing. The ball milling and heat treatment conditions for obtaining amorphous or nanocrystalline alloys were optimised for different alloy compositions. The nano-/amorphous $Mg_{1.9}M_{0.1}Ni$ (M = Ti, Zr, V) alloys produced by continuous milling reveal improved H-sorption kinetics compared to the nanocrystalline Mg_2Ni [10]. Additional knowledge on the H-sorption kinetics in different Mg alloys is important to understand the mechanism of improving the hydrogen storage

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properties by changing the composition and microstructure of the Mg alloys.

The slow hydrogen diffusion in Mg and Mg alloys is known to be the key factor for the unsatisfactory H-sorption kinetics in these materials. Creating defects and microcracks on the surface of the particles and reducing the particle size of Mg (or MgH_2) by reactive mechanical milling (RMM) lead to a shortening of the diffusion distances of the H atoms and thus to a strong improvement of the sorption kinetics in Mg alloys.

The main aim of the present work is to study the influence of the particle size on the H-desorption process (first dehydriding process after reactive mechanical grinding) of $Mg_{87}Ni_3Al_7Mn_3–H_x$, that was mechanically alloyed in a hydrogen atmosphere. The role of the nanocrystal size on the H-desorption kinetics was also investigated.

2. Experimental part

Pure elemental powders of magnesium, nickel, aluminum, and manganese have been used as starting materials. The ball milling was performed with a planetary ball mill (Fritsch P5) with a rotation speed of 300 rpm, ball to powder mass ratio (B/P) of 15/1 under hydrogen gas atmosphere of 5 atm. The samples were handled in a glove box under argon and the vials were sealed under argon atmosphere. Small amounts of the powder were taken from the mill at regular periods of time for morphological, structural and thermal analysis.

The morphology and the microstructure were analyzed by scanning electron microscopy (JEOL 5510 SEM) and X-ray diffraction (XRD) with Cu Kα radiation. Different particle size factions were obtained by sieving the as-milled powders. The sizes of the particles were: (1) $d \leq 5\,\mu m$; (2) $5 < d < 15\,\mu m$; (3) $15 < d < 25\,\mu m$; (4) $25 < d < 63\,\mu m$; and (5) $63 < d < 100\,\mu m$. Two fractions with essentially different size ($5 < d < 15\,\mu m$ and $25 < d < 63\,\mu m$, named fine and coarse, respectively) were selected for the systematic isothermal kinetics study.

The thermal behavior of the alloys was studied by thermogravimetry (TG) and differential scanning calorimetry (DSC), using a Perkin-Elmer TGS-2 and a Mettler differential scanning calorimeter. The dehydriding kinetics of the alloys after RMM were studied by TG under isothermal conditions in pure argon as well as in a hydrogen atmosphere.

3. Results and discussion

SEM analysis of the powders after 15 h RMM reveals particles of different size in the range 1–60 μm, Fig. 1a. A small number of particles with a size between 60 and 100 μm was also observed. On the surface of the larger particles some considerably smaller ones (<1 μm) can be also seen, as well as agglomerates, consisting of much smaller particles (≤1 μm) can be detected, Fig. 1b. SEM of the finest fraction studied (<5 μm) is presented in Fig. 1c.

During reactive mechanical milling in a hydrogen atmosphere of Mg (87 at.%)–Al(7%)–Ni(3%)–Mn(3%), the microstructure and the phase composition of the powder change with the milling time, Fig. 2. The main phases, obtained after 15 h RMM, are MgH_2, Mg, Mn, Ni; Al is most probably dissolved into Mg. From the XRD patterns in Fig. 2, using a full profile fitting procedure based on the Rietveld method, the grain size and the phase content were determined. The alloy milled for 15 h, which is the subject of a systematic hydrogen desorption study, reveals a nanocrystalline microstructure, with an average nanocrystal size of about 8 nm and about 34 wt.% MgH_2. This nanocrystal size does not change during subsequent milling. A negligibly small difference in the mean size of the nanocrystals of the two particles size-fractions, about 9–10 nm for the coarse (25–63 μm) and 7–8 nm for the fine (5–15 μm) fraction, was detected.

Thermogravimetric (TG) analysis of the 15 h milled powder (not sieved), Fig. 3, gives a total hydrogen amount of 2.45 wt.%, which means that RMM for 15 h under the conditions applied in this study leads to partial hydrogenation of the alloy, and confirms the result of the XRD quantitative analysis for the amount of the hydride formed. The evolution of the amount of hydride as a function of the milling time is shown in Fig. 4. It was found that it depends on the time of milling. After 15 h an almost constant value of about 34 wt.% (46 vol.%) hydride was reached, which corresponds to 2.45 wt.% hydrogen. Further milling under these conditions leads to a small increase of the hydride amount, but the rate of the hydride formation markedly decreases.

Whereas conventional polycrystalline MgH_2 decomposes at temperatures above 400 °C, for the alloy studied an essentially lower temperature of hydrogen desorption (decomposition of MgH_2) of about 230 °C was obtained by TG and DSC. A decrease of more than 15° of the dissociation (dehydriding) temperature with the increase of the hydride content was detected, which has to be associated with the different thermodynamic stability of the hydride formed at the different stages of the RMM process. The thermogravimetric experiments were made in pure argon atmosphere (with a low flow rate of argon), therefore we can consider a high driving force for the desorption process. TG analysis was also carried out in a hydrogen atmosphere (1 atm) and was fount to confirm the temperature of hydrogen desorption and the total amount of hydrogen released, obtained during heating in an argon atmosphere.

The DSC study reveals an enthalpy of dehydriding of about 680 J/g alloy. Assigning this enthalpy to the amount of the hydride in the alloy (determined by the TG) for the enthalpy of the hydride decomposition, a value of about 55 kJ/mol H_2 was obtained. This value is substantially lower than the value for pure MgH_2 (75 kJ/mol H_2).

In order to study the influence of the particle size on the dehydriding process TG analysis with a constant heating rate of 5 K/min was carried out with the different particle size

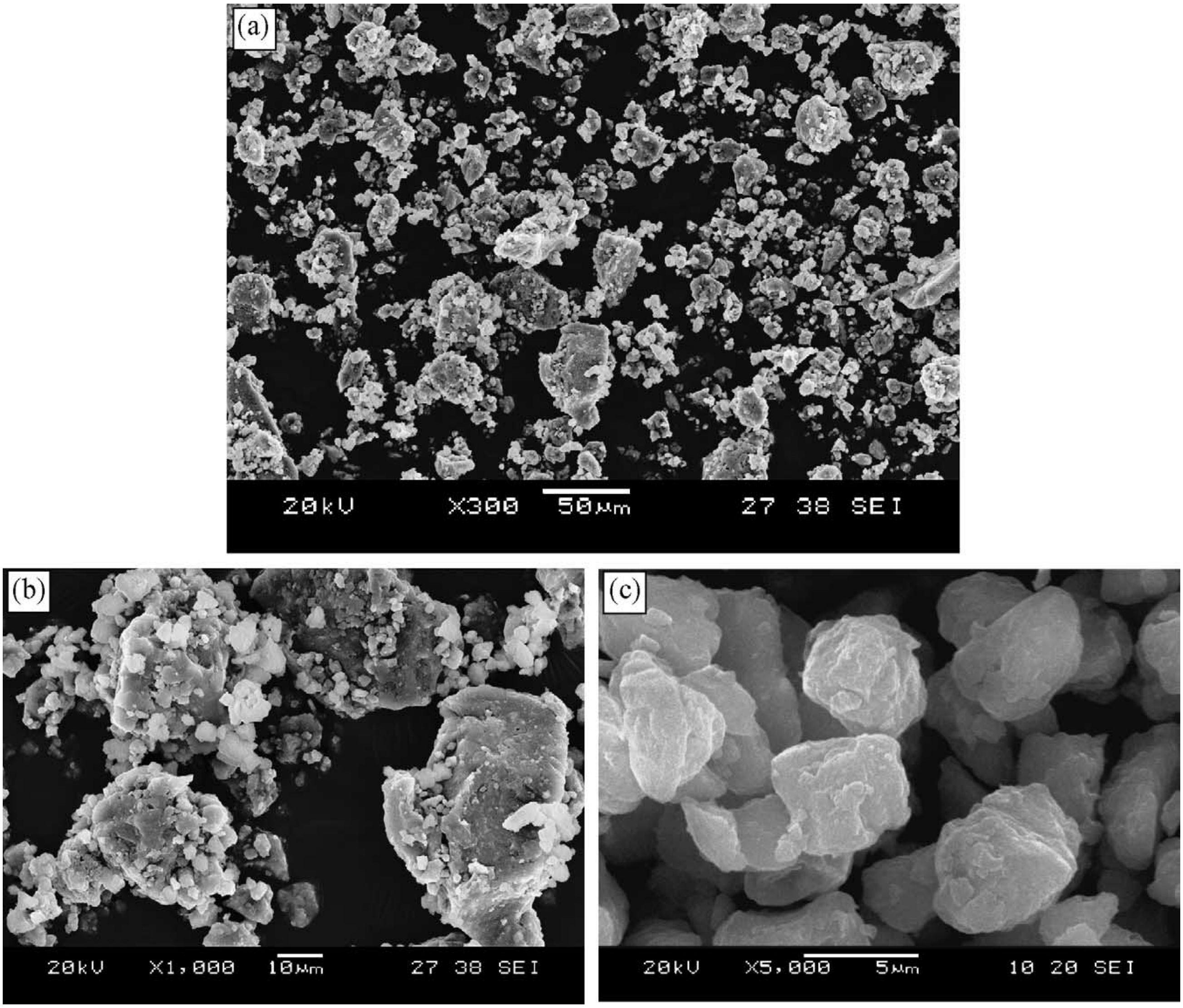

Fig. 1. SEM photograph of the as-milled material (not sieved) (a); of agglomerates (b); and of the finest fraction, separated by sieving with a 5 µm-sieve (c).

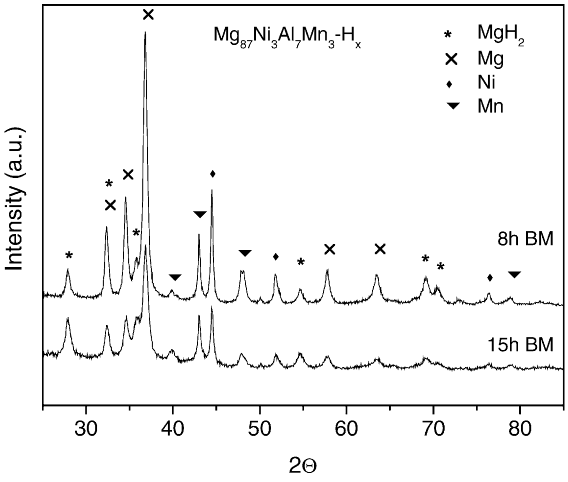

Fig. 2. XRD patterns after different times of milling of Mg (87 at.%)–Al (7 at.%)–Ni (3 at.%)–Mn (3 at.%) in hydrogen atmosphere.

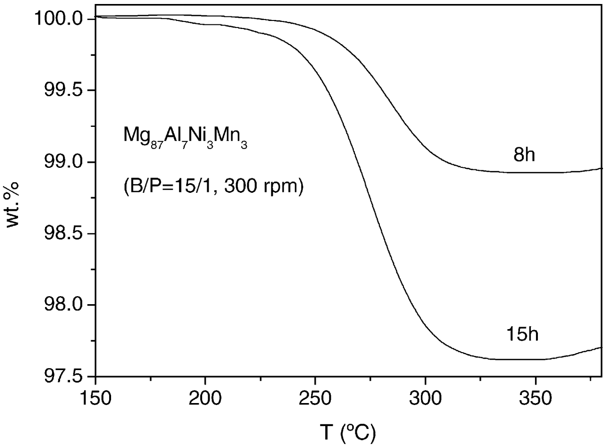

Fig. 3. Thermogravimetric curves of the as-milled powder (after RMM in hydrogen atmosphere for two different milling times); heating rate of 10 K/min.

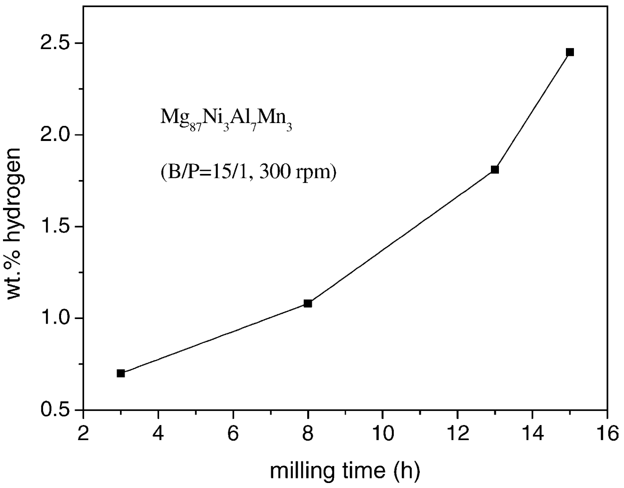

Fig. 4. Amount of hydride formed by RMM in hydrogen atmosphere as a function of milling time.

fractions (5–100 μm), and the total hydrogen amount for each fraction was determined, Fig. 5. A slight lowering of the temperature of H-desorption (about 5°) with the reduction of the particles size was observed. A strong dependence of the hydride amount on the particle size was found, increasing from about 0.5 to more than 4 wt.%, when the particle size decreases from 100 to 5 μm. The uncertainty of the value of the hydrogen content determined for the finest fraction (≤5 μm) is greater, due to the agglomeration of the particles of this size. The stronger surface oxidation of the finest size fraction (despite the protective atmosphere used) presents additional difficulties for the release of hydrogen during heating. Due to the reasons mentioned, slightly larger size-fractions were selected for the following isothermal desorption kinetics study.

Assuming an average particle size for a given size-fraction (for example 20 μm for the fraction $15 < d < 25$ μm) and considering the data presented in Fig. 5, the thickness of the hydride layer on the surface of each particle could be roughly estimated. The values are 1.8 μm for the finer (5–15 μm) and 2.0 μm for the coarser (25–63 μm) fraction. Therefore we can conclude that particles with diameter of about 2 μm would be fully hydrided under the conditions of the RMM process in this study. Moreover, since the amount of the hydride formed during RMM changes very little after 15 h of milling it means that a compact hydride layer is formed and only a small amount of new surfaces are created, which leads to a decrease of the hydrogen capacity. An important conclusion of this result is that producing powder with a particle size of less than the thickness of the impermeable hydride layer (~2 μm (2.0 ± 0.3 μm) in this case) would lead to full hydrogen capacity of the material.

Isothermal thermogravimetric experiments have been carried out in order to study the kinetics of the first dehydriding (after RMM under hydrogen atmosphere) and to obtain information about the mechanism of the process. Two size factions (5–15 μm and 25–63 μm) have been selected and the desorption has been studied at four different temperatures in the range 220–300 °C, Fig. 6. Kinetic curves of the first dehydriding at different temperatures (in argon and hydrogen gas atmosphere; p_{Ar}= 1 atm, p_{H_2} = 1 atm) for the two size-fractions in the coordinates “degree of transformation $\alpha(t)$ versus time t”, Fig. 7, have been deduced from the experimental curves in Fig. 6. From the isothermal kinetic curves $\alpha(t)$ it can be seen that although the smaller fraction desorbs a larger amount of hydrogen for a fixed time than the bigger fraction due to the larger surface area of the finer particles, both fractions desorb hydrogen with similar desorption rate ($d\alpha/dt$) at each temperature studied, Fig. 7.

A number of models have been applied to describe the hydride decomposition kinetics; the first dehydriding reaction after RMG in a hydrogen atmosphere. Different kinetic models, applied to the process studied, are discussed in a number of recent papers [12–15]. Morphological observations of MgH_2 decompositions after partial dehydriding show the metal component to be present on the exterior of the particles [16]. This fact supports the shrinking core model [17] for the

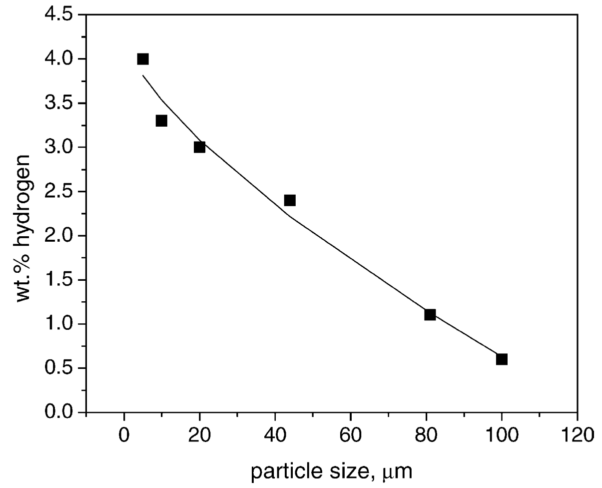

Fig. 5. Amount of H-desorbed vs. particle size (the points represent the middle of the size interval of given fraction).

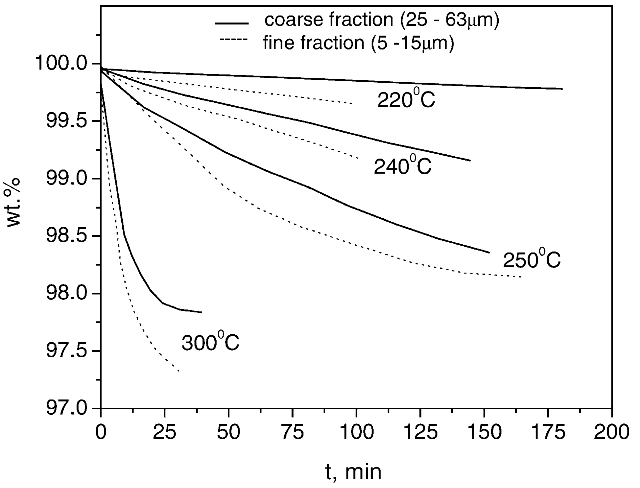

Fig. 6. Experimental isotherms of two different size-factions at different temperatures.

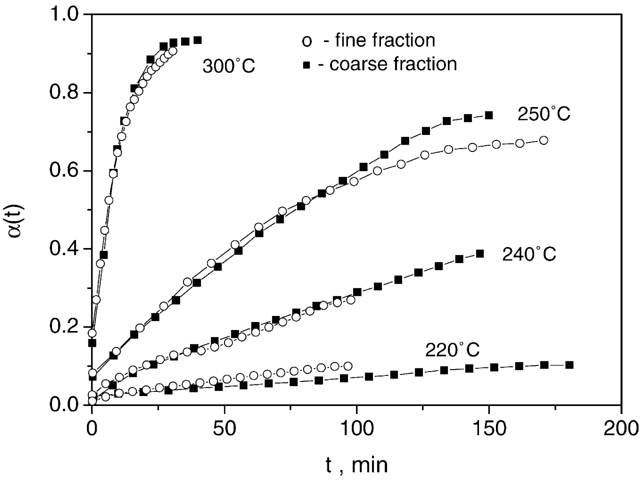

Fig. 7. Degree of transformation (fraction of MgH_2 transformed to Mg) vs. time, $\alpha(t)$ (points: fine fraction; squares, coarser fraction).

decomposition kinetics, controlled by phase boundary motion. In the present study, the kinetic curves, shown in Fig. 7, might be generally fitted by the model based on surface controlled hydrogen desorption reaction: $\alpha = k(T, p)t$, where α is the fraction transformed at time t, $k(T, p)$ is the rate constant, which depends on temperature and pressure. At higher transformation degree $\alpha > 0.6$ (at 250 and 300 °C) a diffusion controlled mechanism was observed: $1 - 2\alpha/3 - (1 - \alpha)^{2/3} = k(T, p)t$. The change of the dehydriding mechanism (rate controlling process) in the advanced stage of the process is illustrated in Fig. 8. The interface controlled two dimensional growth model ($1 - (1 - \alpha)^{1/2} = kt$) describes satisfactorily some of the experimental curves as well. A noticeable difference in the isothermal dehydriding mechanism and kinetics of the two different particle size fractions was not detected. A nucleation and growth controlled mechanism for the MgH_2 decomposition reaction was not observed even at the lower temperatures, most probably due to the presence of a high density of defects on the surface of the particles, created by the RMM.

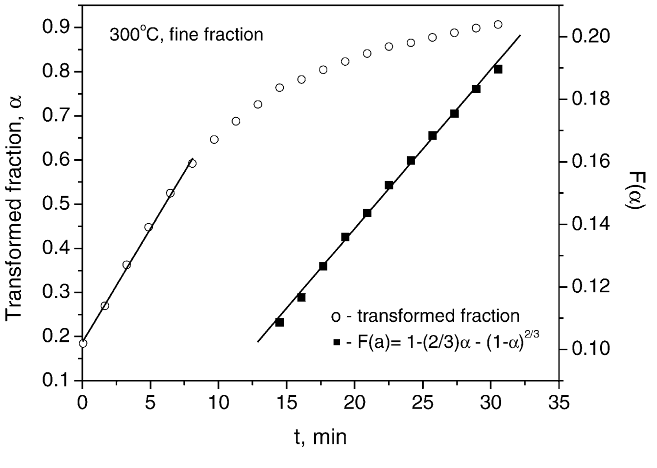

Fig. 8. Transformed fraction α and $F(\alpha)$ versus time of H-desorption (α does not start from zero, because during reaching the temperature of isothermal annealing of 300 °C, the dehydriding reaction has partially taken place).

Isothermal TG analysis at 250 °C with the coarser fraction was also carried out in a hydrogen atmosphere (1 atm). The H-desorption kinetics in this case (at lower driving force compared to the experiment in Ar) are again best described by a kinetic model including a surface controlled reaction. In the advanced stage of the process, diffusion controlled growth takes place. The initial H-desorption rate in a hydrogen atmosphere is similar to that in an argon atmosphere, which is an indication that under these conditions the diffusion is not the rate determining process of the initial dehydriding for $\alpha < 0.6$. From the above kinetics data the conclusion can be drawn that the first dehydriding at all temperatures studied starts with a surface controlled reaction and afterwards switches to a diffusion controlled regime at the advanced stage of the process.

As it was already mentioned, due to very small difference in the nanocrystal size of the two fractions a noticeable difference in their reaction rates (dehydriding rates, $d\alpha/dt$), especially in the first part of the desorption process was not observed. In the advanced stage of the process, the finer fraction shows even some slowing down of the reaction rate, probably due to the stronger oxidation of the sample with more developed surface. From the analysis carried out it was found that the surface area of the particles has a stronger influence on the dehydriding kinetics than the small difference in the nanograin size of the material (from 7–8 to 8–9 nm).

The kinetic analysis realized at different temperatures of H-desorption allowed the activation energy of the dehydriding process to be determined. The activation energies of the initial dehydriding (surface controlled growth), 100–105 kJ/mol, and of the diffusion controlled growth, 105–115 kJ/mol, were obtained from the temperature dependence of the rate constants in the kinetic equations. The finer fraction shows slightly lower activation energy, which has to be attributed to the finer microstructure. Both values are higher compared to those obtained for dehydriding of nano-MgH_2 with metal oxide catalysts controlled by interface growth, 62–72 kJ/mol [9], but lower than the dehydriding activation energies of conventional polycrystalline as well as nanocrystalline MgH_2 without catalyst, 120–142 kJ/mol [18]. It has to be pointed out that the particles size in the above mentioned study [9] (<1 μm) is essentially smaller than the critical passive (impermeable) hydride layer determined by us (about 2 μm). Therefore, diffusion controlled mechanism was not observed.

4. Conculsions

It was found that during RMM of Mg–Ni–Al–Mn in a hydrogen atmosphere of 5 atm, the amount of the hydride (mainly β-MgH_2) increases during the first 15 h and then reaches an almost constant value of about 34 wt.%. The thermal stability of the hydride is substantially lower (temperature of decomposition of 230 °C) than that of the conventional pure MgH_2 and also slightly lower than that of nanocrystalline MgH_{2+} different catalysts. The enthalpy of H-desorption determined, 55 kJ/mol, is substantially lower than that of MgH_2 (75 kJ/mol H_2).

The influence of the particle and grain sizes on the first dehydriding reaction was studied. The finer particle fractions contain an essentially larger amount of MgH_2 than the coarser ones, as the thickness of the hydride layer was estimated to be approximately the same for all particles, about 2 μm. This value was found to be close to the critical thickness of the impermeable hydride layer formed under the experimental conditions of RMM applied in the present study.

Isothermal kinetics analysis reveals that the first dehydriding reaction in nanocrystalline $Mg_{87}Al_7Ni_3Mn_3$–H_x is initially surface controlled. In the advanced stage of the desorption process ($\alpha > 0.5$–0.6), the diffusion of hydrogen atoms through the Mg layer becomes the rate determining process and the reaction mechanism changes to diffusion controlled. Some of the dehydriding kinetics curves (for $\alpha < 0.5$–0.6) can be also satisfactorily described by interface controlled growth of the reaction product. The activation energy of dehydriding obtained for the surface controlled stage is 100–105 kJ/mol and for the diffusion controlled step is 105–115 kJ/mol. These values are lower than those for dehydriding of polycrystalline as well as nanocrystalline MgH_2 without catalyst [18], but larger than the value for nanocrystalline MgH_2 with metal oxide catalysts [9].

Finally, the present study shows that optimization of the milling conditions is important in order to obtain by RMM in a hydrogen atmosphere a larger amount of hydride, possessing fast H-sorption kinetics.

Acknowledgements

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