

Improvement approaches of hydrogen sorption process in magnesium

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Materials

ABSTRACT

Purpose: of this paper is to study the possibility of use of magnesium hydrides as energy carriers. The hydride, MgH_2 , can store up to 7.6 wt. % of hydrogen, but there are three problems with the application of pure Mg: (a) the rate at which hydrogen absorbs and desorbs is too low; (b) the hydrogen molecules do not readily dissociate at the surface of Mg to generate the hydrogen atoms that diffuse into metal; (c) the hydrogen desorption takes place at high temperature.

Design/methodology/approach: as magnesium can be used as hydrogen storage material is to improve hydrogenation / dehydrogenation process by alloying with other metals such as Ni and Al. Nanocrystalline magnesium based alloys were prepared by ball milling. The milling was carried out with a planetary mill and the effect of Ni and Al addition was investigated by means of thermogravimetry analysis (TGA), X-ray diffraction analysis (XRD) and scanning electronic microscopy (SEM).

Findings: Through this study it was found that the above problems could be solved by forming of small magnesium and magnesium based alloy crystals using ball milling technique. The addition of small amount of nickel, can catalyse the bond breaking / formation of the hydride event at the surface. The alloying with aluminium was shown that the thermodynamical properties -lower desorption temperatures and kinetic of hydrogen sorption process were improved along with improved resistance to O_2 contamination.

Practical implications: The inclusion of Ni and Al into magnesium by mechanical ball milling leads to lower the hydrogen desorption temperature from hydride and kinetic improvement of hydrogen sorption process in magnesium. Addition of Ni and Al to Mg also represents new approach of improvement of materials based on light metals, that can provide promising results for the hydrogen storage applications.

Originality/value: The results presented in this paper contribute to elucidate the hydrogen sorption process in magnesium based alloys for to increase their hydrogen storage capacity. Because the hydrogen has the highest heating value of all chemical fuel and is environmentally harmless, in future it will become the most important energy carrier and magnesium alloys can compete with other materials for to achieve very efficient hydrogen storage systems.

Keywords: Metallic alloys; Magnesium; Hydrogen; Sorption

1. Introduction

Metals can adsorb hydrogen in atomic form and act as hydrogen "sponges" [1]. Nearly 50 metallic elements of the periodic table can adsorb hydrogen in significant quantity and the possible choices of hydrogen storage materials are, therefore,

enormous. Many scientific and engineering studies have been carried out of the absorption/desorption of hydrogen in metals and development of such storage devices [1-3]. If metal hydrides are to become important energy carriers the mass of the system needs to be reduced. This puts severe constraints on the chemical elements which can be used [3-5]. A very promising approach to

forming metallic hydrogen storage materials is to use magnesium. The hydride, MgH_2 , can store up to 7.6 wt. % of hydrogen [4], but there are many problems with the application of pure Mg as concerns hydrogen sorption process [6-9]. The most efficient approach to improve the sorption process appears to be the formation of composites with small grains, preferably on nanometer length scale [10,11], then add small amount of a heavy, catalytically active transition metal on the surface of the small grains [12] and an other light metal that has low affinity to hydrogen, for example aluminium, that competes with hydrogen for the valence electrons of magnesium [13-15]. In this paper we study the effect of ball milling time on the thermodynamics and structural properties of Mg_2Ni mixtures prepared under argon or hydrogen atmospheres. But Mg_2Ni being one of the most successful attempts still require more than 250°C in order to release hydrogen at 1 bar. When alloying with Al the low price is retained and Al adds improved heat transfer to the hydride bed, which is essential for fast dehydrogenation. We also present what are the thermodynamics and kinetics of hydrogen sorption process in Mg-Al and Mg-Ni alloys compared to pure magnesium.

2. Experimental

Mechanical alloying of Mg-Ni and Mg-Al mixtures was performed in a planetary mill (Fritch P5) using stainless steels balls and vials, under 1-6 bars of Ar or H_2 . Mg powder (purity higher than 99.8%), Ni powder (purity 99.9%) and Al powder (purity 99.9%) were used. Mg and Ni in the atomic proportion 2:1 were placed in the milling chamber in the argon atmosphere of a glove box. The ball to powder weight ratio used was 10:1. The milling was performed in two atmospheres: argon (purity 99.995%) at a pressure of 1 bar or hydrogen (purity 99.995%) at a pressure of 6 bar. Their structures were studied by X-ray diffraction (XRD, Philips Electronic Instruments, PW 1710). In order to investigate their thermal stability, samples were milled during 20 to 80 hours and were thermally treated at 200°C during 10 min. under argon atmosphere. Scanning electron microscopy (SEM, Philips Electronic Instruments, 515) was used to observe the microstructure. The samples were placed in a closed system with constant volume under pure hydrogen atmosphere (99.995%) to study the hydrogen absorption kinetics. The amount of absorbed hydrogen was estimated from the decrease of pressure in time and from hydrogen amount obtained in desorption process. The successive hydrogen absorption/desorption kinetic measurements were performed at 250°C (absorption) and 300°C (desorption). The Mg-Al mixtures was also obtained using the above conditions. Their structures were studied by X-ray diffraction and scanning electron microscopy.

3. Results and discussions

The results of the structural evolution of Mg-Ni mixture milled in argon are shown in Figure 1. During the initial period of milling (20 h) the XRD diagram corresponds to both metals used as starting materials. Amorphization of magnesium is observed after 40 h and the intermetallic Mg_2Ni is detected after 50 h of milling. This compound shows a nanocrystalline structure with

the half height width of its peaks increasing with milling time, indicating the reduction of the crystallite size.

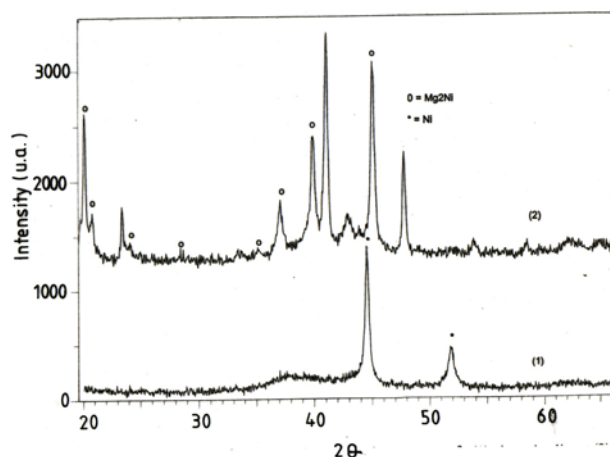


Fig. 1. XRD diagrams of Mg-Ni milled under argon atmosphere : 1-amorphous state; 2-crystalline state

To analyze the thermal stability of the phases, two samples milled during 60 and 80h respectively were thermally treated at 200°C in argon. While crystallization of Mg_2Ni is observed by XRD in the first sample (fig. 2a), the nanocrystallinity of the sample milled for the longer time remains unchanged. The microstructural study of the sample milled 60 h shows that the size of agglomerates increases with thermal treatment (fig. 2b). Inside the particles are homogeneous and close to the initial atomic ratio. The evolution of the X-ray diffractograms with milling time for samples milled under hydrogen atmosphere shown that MgH_2 is formed during the first hours of milling while Mg and Ni are still detected after 20 h of milling. The amount of MgH_2 increases with milling up to 50 h, being consumed by reaction with nickel for longer milling times. In fact, after 80 h the presence of Mg_2NiH_4 is observed. After 80 h of milling XRD shows that this compound is still mixed with Ni. Magnesium that did not react with nickel has been amorphized by the milling. Thermogravimetric analysis of samples milled 80 h show a weight loss of 2.65 wt.% associated to the intermetallic hydride decomposition peak. This value is in good agreement with the hydrogen content determined by other researchers [2,3,9].

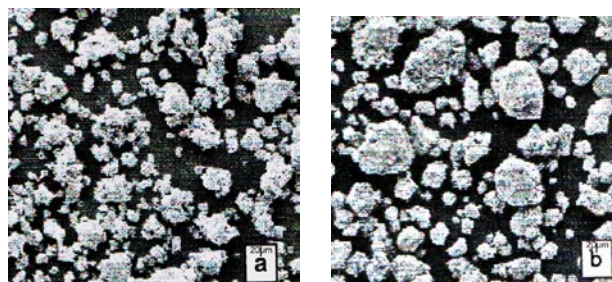


Fig. 2. SEM micrograph of a sample milled 60 h in argon before thermal treatment of Mg_2Ni (a) and after thermal treatment of Mg_2Ni (b)

3.1. Hydrogen sorption in Mg and Mg-Ni alloy

To evaluate the potential of use of these alloys for hydrogen storage, the absorption kinetics of samples milled 50 h under both atmospheres was studied. Samples obtained by milling in argon react with hydrogen after the thermal treatment in vacuum and hydrogen absorption is observed for these samples. Figure 3 shows the absorption curves measured at 250°C with samples milled in hydrogen or milled in argon and then thermally treated.

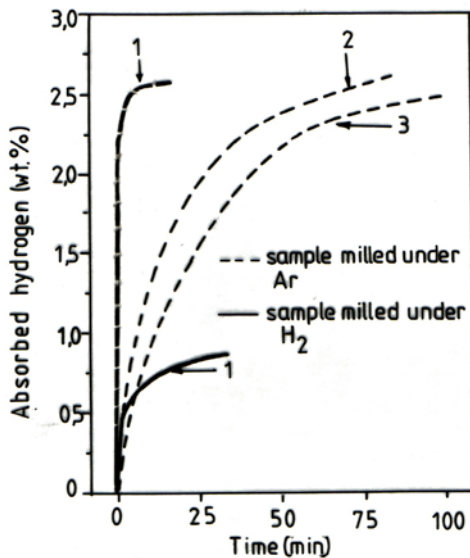


Fig. 3. Hydrogen absorption curves at 250°C of samples milled during 50 h under argon and hydrogen atmospheres: (1-first absorption; 2-second absorption; 3-third absorption)

The maximum hydrogen absorption capacity was achieved for samples milled in argon (2.65 wt. %), much higher than that determined for samples milled in hydrogen (0.84 wt.%). Crystallization of the Mg_2Ni intermetallic phase is enhanced by the initial thermal treatment in vacuum. After hydrogen absorption/desorption cycles this phase, initially nanocrystalline, increases its degree of crystallinity. Samples analyzed by XRD after the third hydrogen absorption have shown patterns corresponding to the hydride phase $MgNi_2H_4$ and unreacted $MgNi_2$. The above results show that the milling of Mg and Ni under argon atmosphere leads to the formation of the intermetallic Mg_2Ni after long periods of milling time.

The material progressively decreases its crystallite size due to fracture of the particles produced by the high-energy impacts of the balls. The crystallite size was determined using the Scherrer equation. The values obtained for samples milled during 50, 60 and 80 hours were 90, 65 and 50 Å, respectively. A slight increase in crystallinity is produced after the treatment performed at 250 °C during 5 h. On the other hand, although the formation of Mg_2Ni by mechanical alloying was observed after 50h of milling, the crystallization of this compound is achieved by thermal treatment at a lower temperature than that reported in the literature [3,4]. Metallic magnesium presents low reactivity with

hydrogen. When comparing the results from both milling atmospheres studied in this work, we observe that unreacted metals remain present in the mixture milled in hydrogen while the reaction has been completed if milling is performed in argon for the same time. Heterogeneous reactions are observed when mechanical alloying is performed under reactive atmosphere (H_2); here the synthesis of hydrides is favored, instead of the formation of the intermetallic Mg_2Ni . After 80 h of milling the total hydrogen content is 2.65 wt.% (lower than the theoretical value of 3.6 wt.% for Mg_2NiH_4). The hydrogen absorption curves measured at 250°C corresponding to the sample milled in argon (Figure 3) show that the Mg_2Ni phase, after partial crystallization by thermal treatment in vacuum at the same temperature, absorbs hydrogen readily, completing the process in about 8 minutes. Further absorption kinetics is slower. This behavior can be related with the evolution of the material. Although it was reported that an improvement in hydrogen absorption kinetics is observed when the ratio Mg_2Ni/Mg increases, the influence of defects masked this effect in our experiments. Moreover, the hydrogen absorption kinetics is slower after successive absorption/desorption cycles due to this structural reconstitution of the material. For samples milled under hydrogen atmosphere the final hydrogen content is lower than that observed in samples milled in argon. Now, we are developing further studies to investigate the precise conditions under which the Mg_2Ni phase is formed and the influence of successive absorption/desorption cycles on the reaction kinetics.

3.2. Hydrogen sorption in Mg-Al alloy

When magnesium is alloying with aluminium the low price is retained and Al adds improved heat transfer to the hydride bed, which is essentially for faster dehydrogenation. Only few studies on hydrogenation/dehydrogenation behaviour of Mg-Al and Mg-Al-Ni alloys have been reported [13-15]. It was found that the thermodynamics and kinetics of Mg-Al and Mg-Al-Ni compared to Mg are improved along with the resistance towards oxygen contamination. Upon hydrogenation the Mg-Al alloy disproportionates under formation of MgH_2 and Al according to the scheme below:



During dehydrogenation Mg and Al reacts and an Mg-Al is recovered. In the hydrogenated state only MgH_2 and Al is present, after dehydrogenation diffraction peaks from MgH_2 and Al are absent and only those corresponding an Mg-Al alloy (mainly β -phase) are present.

The reason for disproportionation of Mg-Al alloy during hydrogenation may be explained by a relatively high thermodynamic stability of MgH_2 compared to that of the alloy, combined with a relatively low stability of a Mg-Al-H compound. Formation of AlH_3 will not occur during hydrogenation of Mg-Al since the temperature applied to reach acceptable kinetics for MgH_2 exceeds the decomposition temperature of AlH_3 unless a very high hydrogen pressure is applied.

The theoretical gravimetric hydrogen storage capacity, $\rho_m(H_2)$ of Mg-Al alloys can be easily estimated from reaction (1). It is generally known that magnesium does not promote dissociation of hydrogen molecules. It is difficult to judge to which degree the

presence of Al in Mg-Al improves the ability to dissociatively absorb hydrogen compared to pure Mg. We have studied the effect of higher Al concentrations on the hydrogenation kinetics of Mg-Al alloys. The results are shown in Figure 4. As seen in the figure the hydrogenation behaviour of unmilled Mg and ball milled Mg-Al (9:1) are more or less identical. Thus apparently no improvements of the kinetics have been achieved at a 10 at.% concentration of Al. For higher Al concentrations the rate of hydrogenation was higher compared to pure Mg. According to Figure 4, it is evident that higher concentrations of Al leads to significantly improved hydrogenation kinetics, especially for the sample with a Al content > 25 at.% Al. The same effect was observed for the dehydrogenation kinetics. Hydrogen diffusion in Mg-Al and Mg-Ni alloys is significantly better than for MgH₂.

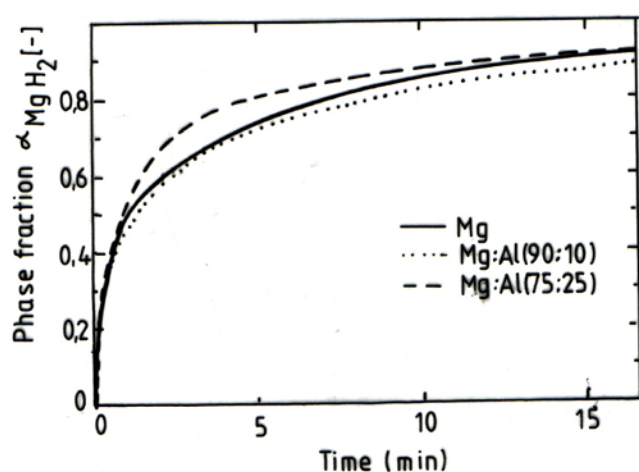


Fig. 4. Hydrogenation kinetics of pure unmilled Mg compared with Mg-Al compounds with varying content, ball milled for 40h. Hydrogenation performed at 300°C and H₂ pressure of 6 bar

4. Conclusions

Magnesium can be used as hydrogen storage material if is alloyed with other metals such as Ni and Al that improve the hydrogen sorption process. Ni addition to magnesium produces a catalytic effect and helps hydrogen molecules to dissociate at the surface of Mg and to generate the hydrogen atoms that then diffuse into metal. The desorption temperature of Mg₂Ni alloy is about 50 degrees lower than for pure Mg, but this is still far from low enough. The addition of Ni to Mg that is a heavy transition metal greatly reduces the storage capacity, down to 3.6% from 7.6% in pure Mg. A better solution is to add small amount of Ni for catalytic effect and then a bigger amount of a light metal that has low affinity to hydrogen, such as Al, which to reduce the mass of the system and thus the magnesium hydrides can become important energy carrier. Hydrogenation/dehydrogenation process of Mg-Ni and Mg-Al alloys suggests that these alloys have improved kinetics compared to pure magnesium.

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