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Hydrogen sorption properties of the nanocomposite 90 wt% Mg_2Ni+10 wt% V

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Abstract

The absorption–desorption characteristics of the nanocomposite 90 wt% Mg_2Ni+10 wt% V obtained by mechanical alloying under argon or hydrogen atmosphere have been investigated. The effect of vanadium, the activation time and the gas medium during the milling on these characteristics have been shown. The absorption capacity of the sample activated for 30 min under argon is found to be 1.94% at $T=573$ K and $P=1$ MPa, whereas for the hydrogen-activated sample the capacity is 2.3% and some absorption is observed even at room temperature. The hydrogen sorption properties of the $Mg_2Ni+10\%$ V composite are compared with those of an alloy with the composition $Mg_2Ni_{0.9}V_{0.1}$.

Keywords: Hydrogen storage materials; Intermetallics; Gas–solid reaction; Mechanical alloying

1. Introduction

Magnesium and its alloys are promising materials for hydrogen storage. The high absorption capacity (7.6%) of Mg can only be reached after activation at high temperatures and pressures. The intermetallic compound Mg_2Ni can absorb up to 3.6% H_2 with formation of Mg_2NiH_4, but the hydriding temperature is again too high for practical application.

Mechanical alloying in an inert atmosphere has been used for preparing composites with improved absorption–desorption properties [1]. Mechanical grinding results in enhanced reactivity of the surface due to the formation of defects. Addition of transition metals (Ce, Ti, Nb, Fe, Co and Ni [2]), oxides [3,4] and intermetallic compounds such as $LaNi_5$, $MmNi_5$ or YNi_5 [5] has been used to facilitate the hydriding and dehydriding processes. The transition metals on the magnesium surface catalyze the dissociative chemisorption of hydrogen. Some of them such as Ce, Ti and vanadium form hydrides which 'pump' hydrogen from the surface to the bulk of Mg or Mg_2Ni. The hydride of vanadium has a small unit cell parameter, due to which of all the metals it exhibits the highest volumetric hydrogen density and diffusivity [6].

It has been shown in the literature that the composite MgH_2+5 at% V obtained by mechanical alloying has a high capacity and improved hydriding kinetics due to the catalytic role of vanadium, the increased specific surface area and the presence of defects after mechanical alloying [7].

Mechanical grinding under hydrogen has been applied to systems such as ZrNi–H [8], TiNi–H [9], and Mg_2Ni–H [10]. In several recent papers [11–13] it is shown that reactive mechanical grinding can also be used for improving the hydriding kinetics of Mg-based materials. The result of mechanical grinding is a considerable decrease in size of the magnesium particles [14].

The present work is aimed at studying the absorption and desorption properties of the nanocomposite 90 wt% Mg_2Ni+10 wt% V prepared by mechanical alloying under argon or hydrogen and elucidating the role of the gas medium during grinding, the time of mechanical alloying and the effect of vanadium on these properties. The absorption–desorption characteristics observed have been

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compared with those of an alloy with the composition $Mg_2Ni_{0.9}V_{0.1}$.

2. Experimental

For the synthesis of Mg_2Ni, a mechanical mixture of Mg and Ni with a 99.9% purity and a Mg:Ni atomic ratio of 2.05:1 was tabletted and heated under argon at 823 K for 120 h. A certain Mg excess was chosen to compensate for the Mg loss due to evaporation of magnesium and formation of $MgNi_2$. The 90% Mg_2Ni+10% V composite was obtained by mechanical alloying under argon or hydrogen in a Fritsch Pulverisette 5 planetary mill with stainless steel balls, 10 mm in diameter, the vessel having a volume of 75 cm^3. The experiments were performed with a 10:1 weight ratio between the balls and the samples, a rotation rate of 200 rpm and grinding durations of 30 min and 1 h.

A mechanical mixture of the elements was tabletted and heated under argon at T=823 K for 72 h and T=923 K for an additional 72 h in order to obtain $Mg_2Ni_{0.9}V_{0.1}$. The phase composition of all samples was controlled by X-ray phase analysis using Cu Kα radiation. The absorption–desorption properties towards hydrogen of the mechanically alloyed composites Mg_2Ni+10% V and the alloy $Mg_2Ni_{0.9}V_{0.1}$ were studied by a volumetric method described in Ref. [15]. The hydriding reaction proceeded at a pressure of 1 MPa and T=573, 473, 423, 373 K and room temperature. Dehydriding occurred at 573 K and a pressure of 0.15 MPa. The samples were also characterized by microprobe analysis with a CAMECA 3x-100 instrument, scanning electron microscopy and particle size measurements performed in ethanol using a Malvern 2000 device.

3. Results and discussion

Fig. 1 presents the X-ray diffraction patterns of the initial phases investigated. The synthesized Mg_2Ni contains traces of Ni, MgO and the parasite phase $MgNi_2$. In the alloy $Mg_2Ni_{0.9}V_{0.1}$ there is also some unreacted vanadium. The composite Mg_2Ni+10% V mechanically alloyed for 30 min in a hydrogen atmosphere produces no peaks belonging to a hydride phase, which indicates that the grinding time is not sufficient to form a hydride.

Comparison of the kinetic hydriding curves of the composites alloyed under argon for 30 min and 1 h under a pressure of 1 MPa at different temperatures shows that the shorter time of grinding leads to a higher absorption capacity (Figs. 2 and 3). Obviously, when the duration of grinding is longer, the probability for Mg to be oxidized, increases. This is probably the reason why the composite subjected to 1 h grinding under argon absorbs hydrogen more slowly and does not reach the capacity of the composite having been ground for only 30 min. The absorption curves of the composite ground under hydrogen for 30 min which are given in Fig. 4 show hydrogen absorption even at room temperature, the hydriding rate being higher than that of the sample ground under argon. The data on $Mg_2Ni_{0.9}V_{0.1}$ shown in Fig. 5 reveal a maximum absorption capacity of 2.41% at a temperature of 573 K and a pressure of 1 MPa. A certain amount of hydrogen is also absorbed at room temperature and the same pressure.

The dehydriding temperature of the samples under consideration is relatively high. At T=573 K and P=0.15 MPa, the fastest desorption is observed with the composite Mg_2Ni+10% V mechanically alloyed in a hydrogen at-

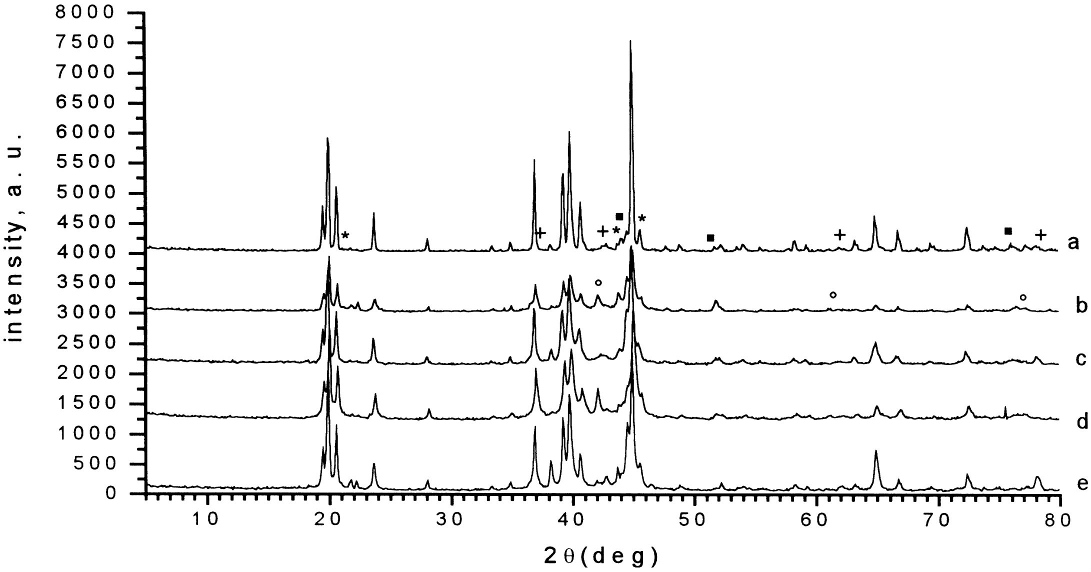

Fig. 1. X-ray diffraction patterns of: (a) Mg_2Ni; (b) 90 wt% Mg_2Ni–10 wt% V ball-milled for 30 min under argon; (c) 90 wt% Mg_2Ni–10 wt% V ball-milled for 30 min under H_2; (d) 90 wt% Mg_2Ni–10 wt% V ball-milled for 1 h under argon; (e) $Mg_2Ni_{0.9}V_{0.1}$ ball-milled for 30 min under argon. (*) $MgNi_2$, (■) Ni+MgO, (○) V and unmarked Mg_2Ni.

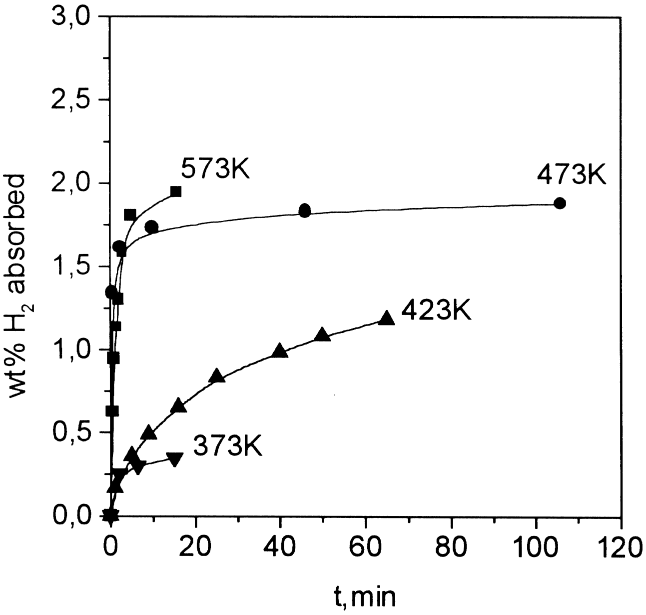

Fig. 2. Time-dependences of the wt% of hydrogen absorbed at $P=1$ MPa and different temperatures for the composite Mg_2Ni–10 wt% V ball-milled for 30 min under argon.

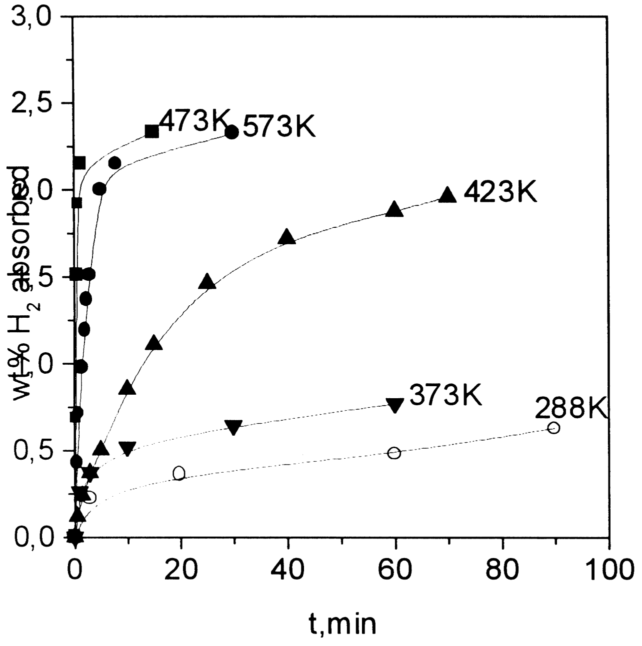

Fig. 4. Time-dependences of the wt% of hydrogen absorbed at $P=1$ MPa and different temperatures for the composite Mg_2Ni–10 wt% V ball-milled for 30 min under hydrogen.

mosphere. The desorption rate in this case is comparable with that of the alloy $Mg_2Ni_{0.9}V_{0.1}$ (Fig. 6).

The kinetic curves display a higher rate of hydriding at 473 K as compared to the rate at 573 K. A similar effect has been established by Song et al. [16] during hydriding of Mg_2Ni. These authors reported that the hydriding rate around the temperature of polymorphic transition of Mg_2NiH_4 (508 K) is higher than that at higher temperatures. This may be attributed to a possible change of the rate-controlling step of hydriding around 508 K.

The results of microprobe analysis show the presence of Ni and V clusters on the surface of Mg_2Ni and $Mg_2Ni_{0.9}V_{0.1}$. They are in good agreement with the data reported by Schlapbach et al. [17]. Surface analysis with a scanning electron microscope shows that the particles of the composite ground under hydrogen are smaller and

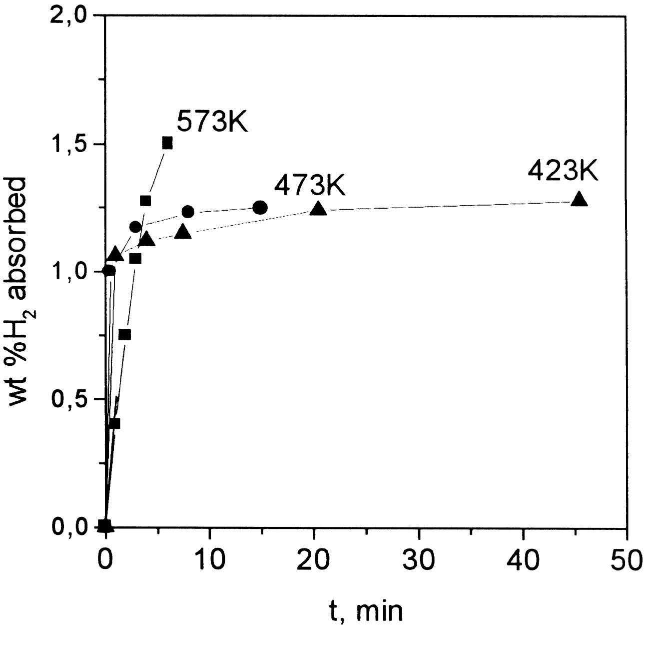

Fig. 3. Time-dependences of the wt% of hydrogen absorbed at $P=1$ MPa and different temperatures for the composite Mg_2Ni–10 wt% V ball-milled for 1 h under argon.

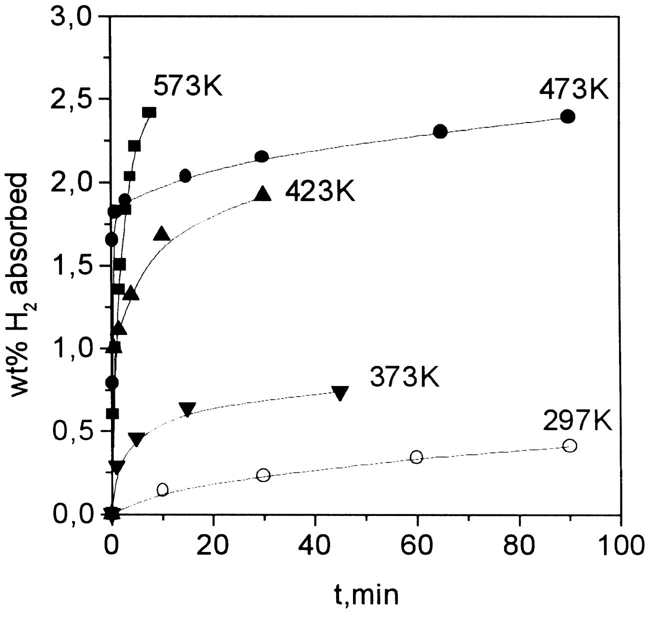

Fig. 5. Time-dependences of the wt% of hydrogen absorbed at $P=1$ MPa and different temperatures for $Mg_2Ni_{0.9}V_{0.1}$.

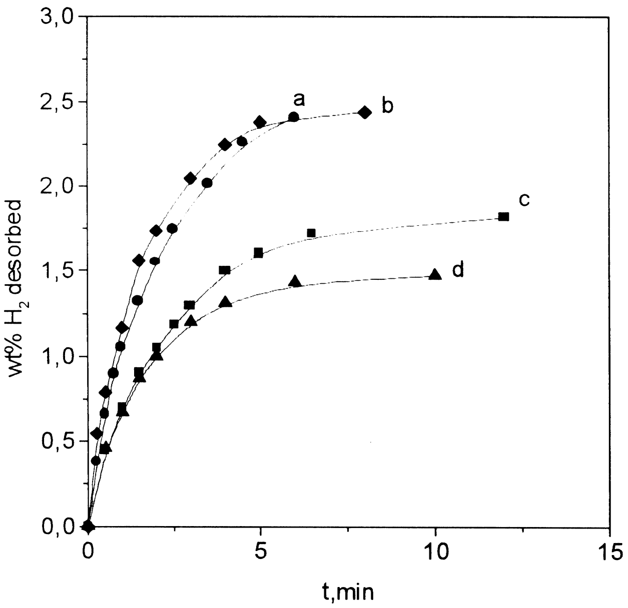

Fig. 6. Time-dependences of the wt% of hydrogen desorbed at P=0.15 MPa and T=573 K for (a) $Mg_2Ni_{0.9}V_{0.1}$; (b) composite Mg_2Ni–10 wt% V ball-milled under hydrogen; (c) composite Mg_2Ni–10 wt% V ball-milled for 30 min under argon; (d) composite Mg_2Ni–10 wt% V ball-milled for 1 h under argon.

close in size, whereas those of the sample ground under argon are larger and not so uniform.

The data on the particle size distribution (Table 1) obtained with and without ultrasound lead to an analogous conclusion. Mechanochemical alloying in a reactive medium is associated with formation of a more finely dispersed material. The samples ground under argon tend to form agglomerates. The application of ultrasound results in formation of smaller particles, which indicates that some of the agglomerates deaggregate. The sample Mg_2Ni+10% V alloyed mechanically under argon for 1 h shows no change in particle size distribution upon ultrasonic treatment. Two hypotheses may be proposed for explaining this fact either the number of agglomerates is very large and the bonds between the small particles are too strong to be broken by the ultrasonic waves or there are no agglomerates at all. SEM analyses are now in progress to confirm one of this hypotheses.

4. Conclusion

On the basis of the experimental data obtained it could be concluded that addition of vanadium and mechanical alloying under argon or hydrogen improve the hydriding kinetics of Mg_2Ni. Activation in a hydrogen medium leads to absorption properties comparable with those of the alloy $Mg_2Ni_{0.9}V_{0.1}$. Prolonged grinding in an inert medium deteriorates the absorption properties of the composite due to the formation of larger particles and additional oxidation of the surface.

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Table 1
Particle size distribution with and without application of ultrasound (US)

Sample	$d_{0.1}$	$d_{0.5}$	$d_{0.9}$	Span $(d_{0.9}-d_{0.1})/d_{0.5}$
90% Mg_2Ni+10% V 30 min (H_2)	2.536 US 2.457	4.071 3.867	8.297 7.657	1.415 1.344
90% Mg_2Ni+10% V 30 min (H_2), hydrided	US 1.808	2.453	4.680	1.171
90% Mg_2Ni+10% V 30 min (Ar)	2.617 US 1.543	12.365 9.021	45.599 34.469	3.476 3.650
90% Mg_2Ni+10% V 30 min (Ar), hydrided	2.905 US 1.616	13.208 8.836	54.129 30.687	3.878 3.290
90% Mg_2Ni+10% V 1 h (Ar)	US 2.065	8.780	36.226	3.891

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