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Addition of 3d-metals with formation of nanocomposites as a way to improve the hydrogenation characteristics of Mg_2Ni

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Abstract

The hydrogen absorption–desorption characteristics of a composite material containing 85 wt.% Mg_2Ni, 10 wt.% V and 5 wt.% Ti, obtained by mechanical alloying in a planetary mill under argon have been investigated. The experimental data on the kinetics of hydriding and dehydriding and the absorption capacity values established at various temperatures and hydrogen pressures have been compared with those of a previously studied composite obtained by the same method but containing no titanium. It has been shown that the presence in the composite of a second hydride-forming 3d-metal leads to an enhanced absorption capacity and improved hydriding and dehydriding kinetics. The 85 wt.% Mg_2Ni–10 wt.% V–5 wt.% Ti composite has shown a significant hydrogen absorption at room temperature. The improved characteristics of the Ti-containing composite are attributed to the formation, along with Mg_2NiH_4 and VH_x, of a third hydride, TiH_x, which increases the interface and facilitates both nucleation and back diffusion of hydrogen from the sample.

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

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1. Introduction

Magnesium and its alloys and composites are promising materials for hydrogen storage. The advantages of Mg consist in its high absorption capacity (7.6 wt.% H_2), low cost and abundance in the earth's crust. However, the capacity can only be reached after hydriding at high temperatures and pressures, the hydride MgH_2 formed being too stable for practical application.

Mg-based hydrogen storage intermetallics form hydrides which are more unstable than MgH_2. The hydrogen capacity of these alloys is lower than that of pure magnesium. Among alloys having appropriate capacity values, the intermetallic compound Mg_2Ni ranks first. It is lighter and cheaper than the $LaNi_5$-type alloys which have found the widest application as hydrogen storage materials. Upon hydrogenation Mg_2Ni forms the hydride phase Mg_2NiH_4 whose hydrogen content (3.6 wt.%) is more than twice as high as that of $LaNi_5H_6$ (1.5 wt.% H_2). Besides, in contrast to magnesium and a series of other hydrogen storage systems, Mg_2Ni is more stable in air. Its major disadvantages are the relatively high activation and desorption temperatures (about 573 K) and poor hydriding–dehydriding kinetics [1].

In order to overcome the above disadvantages, ball-milling preparation of Mg_2Ni was proposed and adopted in almost all studies during the last decade [1–3]. The observed easy activation and improved hydriding kinetics are ascribed to the appearance of: (i) a nanocrystalline or amorphous state of the material rich in dislocations and special defects [2,4] and (ii) clean and highly reactive surfaces, which leads to an increase of the hydrogen absorption rate [5].

During the past years different additives were used for improving the hydriding–dehydriding characteristics of Mg_2Ni, formation of nanocomposites being achieved by mechanical alloying. Thus, already in 1995 Zaluski et al. [6] established the favourable catalytic effect of the addition of Pd, which was confirmed more recently by Janot et al. [7]. However, for economic reasons most researchers preferred developing composite materials with the participation

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of less expensive additives to Mg_2Ni. Thus, it was shown that the kinetics of hydrogen desorption from nanocrystalline Mg_2Ni, could be improved significantly after addition of about 5–10 wt.% fullerene C_{60} or graphite [7,8].

Sato et al. [9] have established that during ball-milling of Mg_2Ni with up to 4 at.% Al, a certain amount of aluminum (maximum 1 at.%) is incorporated into the crystal lattice of the intermetallic compound. The substitution exercises a certain effect on the hydriding–dehydriding properties which, however, is progressively reduced by cycling. In a recent study Gasiorowski et al. [10] used elemental Mg, Ni, Al and Mn as starting substances for obtaining nanocrystalline samples of $Mg_{2-x}M_xNi$ (M = Al or Mn) by ball-milling with subsequent annealing at 450 °C. These authors established that up to $x = 0.25$, products isostructural with the hexagonal Mg_2Ni were obtained. However, when $x = 0.5$, a crystalline phase of $Mg_{1.5}M_{0.5}Ni$ with a CsCl-type cubic structure was formed. In all cases, partial replacement of Mg by Al or Mn led to an important decrease in hydrogen absorption capacity.

Hydrogen storage alloys of the Mg–Ni–Cu system obtained by combustion synthesis were also studied [11]. It was shown that an alloy with the composition $Mg_2Ni_{0.75}Cu_{0.25}$ stored 1.7 wt.% hydrogen at 473 K with a low hydriding rate. A significant improvement of the hydrogenation properties was observed with samples prepared by mechanical alloying in which Mg was partially replaced by Ag. Wang et al. [12] established that the alloy $Mg_{1.8}Al_{0.2}Ni$ preserved the structure of Mg_2Ni and when hydrided at $P = 1$ MPa the absorption capacity reached 2.2 wt.% at 150 °C.

In a series of papers [13–18] it was shown that the presence of transition metal additions in nanocomposites obtained by mechanical alloying facilitated the hydriding and dehydriding of magnesium. It was of interest to see how far these additives were also able to affect the hydrogenation processes of Mg_2Ni. This was made in a previous paper of the authors [19] dealing with the hydrogen sorption properties of the nanocomposite 90 wt.% Mg_2Ni–10 wt.% V prepared by ball milling under argon or hydrogen. It was shown that the hydriding–dehydriding kinetics of this nanocomposite were improved as compared to the kinetics corresponding to pure Mg_2Ni. After activation under hydrogen some absorption was observed even at room temperature. The favourable effect of vanadium addition was attributed to the formation of the hydride VH_x belonging to the binary hydrides with a varying stoichiometry which may, at the expense of their hydrogen content, “pump” hydrogen to the Mg_2Ni surface.

The results obtained with vanadium addition permit the assumption that further improvement of the absorption–desorption characteristics of Mg_2Ni can be achieved on adding, to the Mg_2Ni-based composite, one more 3d-metal able to form a hydride of the type MH_x. This second metal in the present paper was titanium. The investigation was carried out on a composite of 85 wt.% Mg_2Ni–10 wt.% V–5 wt.% Ti an the data obtained on its hydrogenation properties were compared with those of the 90 wt.% Mg_2Ni–10 wt.% V composite studied in Ref. [19].

2. Experimental

Powdery magnesium, nickel, vanadium and titanium with a 99.9% purity were used for preparing both the intermetallic compound Mg_2Ni and its composite with V and Ti. For the synthesis of Mg_2Ni, a mechanical mixture of Mg and Ni in a 2.05:1 atomic ratio was tabletted and heated under argon at 823 K for 120 h. A certain excess of Mg was chosen to compensate for the magnesium loss due to evaporation and undesired formation of $MgNi_2$. The 85 wt.% Mg_2Ni–10 wt.% V–5 wt.% Ti composite was obtained by mechanical alloying under argon 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 sample, a rotation rate of 200 rpm and grinding duration of 30 min.

The absorption–desorption properties of the composite were determined by a volumetric method described in Ref. [20]. Hydrogen absorption proceeded at a pressure of 1 MPa and temperatures in the range 293–573 K. Desorption occurred at 573 K and a pressure of 0.15 MPa. The phase composition of the hydrided and dehydrided composite as well as the structure of the intermetallic Mg_2Ni were controlled by X-ray phase analysis using Cu Kα radiation. Electron microprobe characterization of the initial composite was performed with a CAMECA SX-100 instrument.

3. Results and discussion

The kinetic curves of hydrogen absorption by the composite 85 wt.% Mg_2Ni–10 wt.%V–5 wt.% Ti at different temperatures and a pressure of 1 MPa are shown in Fig. 1.

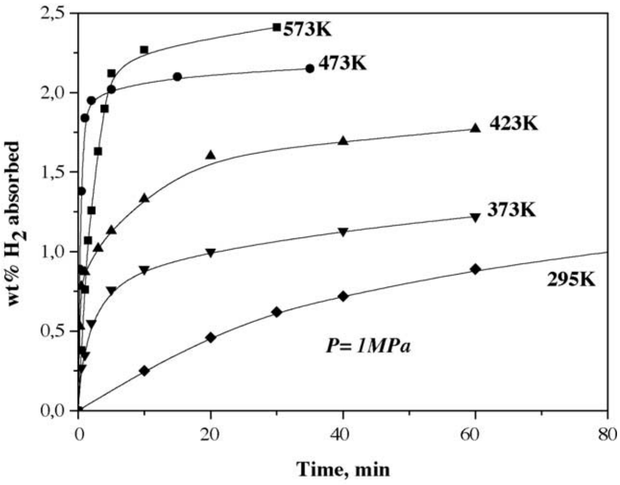

Fig. 1. Kinetic curves of hydriding of the composite 85 wt.% Mg_2Ni–10 wt.% V–5 wt.% Ti at $P = 1$ MPa and different temperatures.

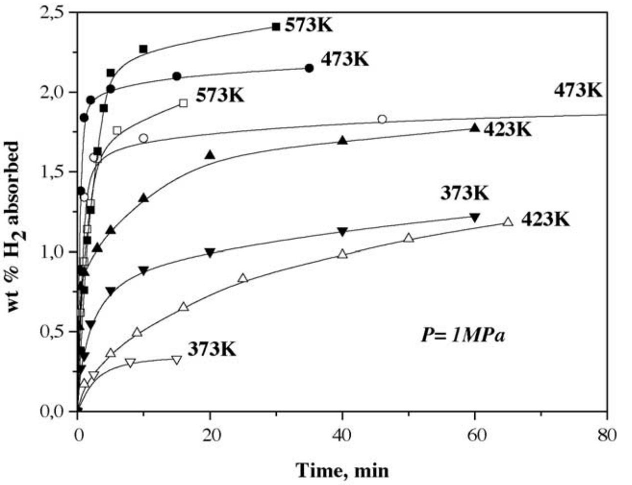

Fig. 2. Kinetic curves of hydriding of the composites 85 wt.% Mg_2Ni–10 wt.%V–5 wt.% Ti and 90 wt.% Mg_2Ni–10 wt.% V at $P = 1$ MPa and different temperatures—(i) 573 K: (■) 85 wt.% Mg_2Ni–10 wt.% V–5 wt.% Ti, (□) 90 wt.% Mg_2Ni–10 wt.% V; (ii) 473 K: (●) 85 wt.% Mg_2Ni–10 wt.% V–5 wt.% Ti; (○) 90 wt.% Mg_2Ni–10 wt.% V; (iii) 423 K: (▲) 85 wt.% Mg_2Ni–10 wt.% V–5 wt.% Ti, (△) 90 wt.% Mg_2Ni–10 wt.%V; (iv) 373 K: (▼) 85 wt.% Mg_2Ni–10 wt.% V–5 wt.% Ti, (▽) 90 wt.% Mg_2Ni–10 wt.%V.

Comparison with the curves obtained under the same conditions in Ref. [19] for the composite 90 wt.% Mg_2Ni–10 wt.% V (Fig. 2) shows that the addition of titanium as a second 3d-metal has a pronounced catalytic effect. This effect is illustrated by the higher absorption capacity of the composite containing both V and Ti as well as by its significant hydrogen uptake (more than 0.8 wt.% after 1 h hydriding) at room temperature. The data obtained for both composites at all hydriding temperatures in the range 373–573 K also show improved absorption kinetics of the Ti-containing sample, especially at 423 and 373 K.

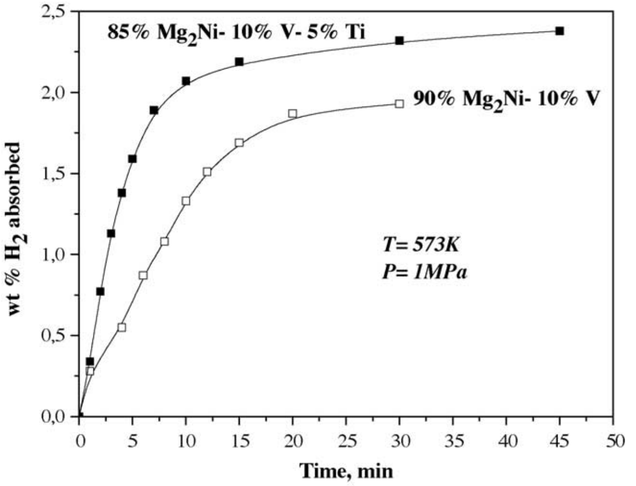

Fig. 3. First cycle of hydriding of: (■) 85 wt.% Mg_2Ni–10 wt.% V–5 wt.% Ti and (□) 90 wt.% Mg_2Ni–10 wt.% V at $P = 1$ MPa and $T = 573$ K.

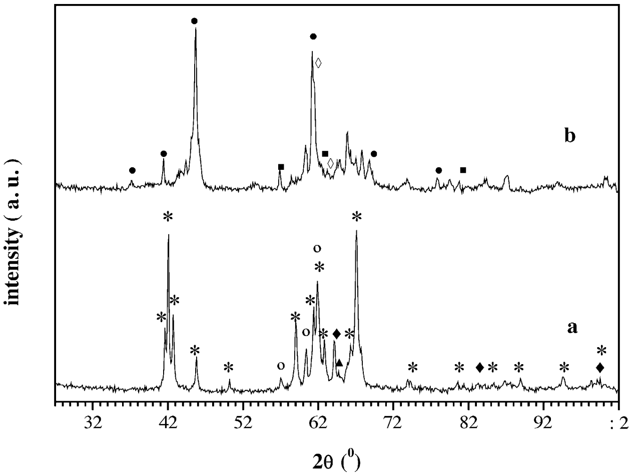

Fig. 4. X-ray patterns of the composite 85 wt.% Mg_2Ni–10 wt.% V–5 wt.% Ti: (a) as-prepared and (b) after hydriding. (*) Mg_2Ni, (○) Ti, (◊) V, (▲) MgO, (●) Mg_2NiH_4, (■) $TiH_{1.92}$ and (♦) $VH_{0.8}$.

The favourable effect of the addition of two 3d-metals is also clearly evidenced by the data presented in Fig. 3 concerning the first cycle of hydriding. Comparison in behaviour of samples containing V and V + Ti, respectively, as additives to the corresponding Mg_2Ni-based composites, shows improved hydriding kinetics and a higher absorption capacity in the case of double addition. It is worth noting that the addition of Ti to the V-containing composite is accompanied by a 5% decrease in the Mg_2Ni concentration. Obviously, the compensation for the reduced Mg_2Ni content, which is mainly responsible for the hydrogen storage, is excessively ensured by the catalytic effect of the second 3d-metal. Similarly to the catalytic action of vanadium established previously [19], that of titanium can be explained by the formation of a nonstoichiometric hydride, TiH_x. The X-ray patterns of the composite 85 wt.% Mg_2Ni–10 wt.% V–5 wt.% Ti before and after hydriding (Fig. 4) show that hydrogen uptake is accompanied by formation of three hydrides, Mg_2NiH_4, $VH_{0.8}$ and $TiH_{1.92}$. Their presence affects favourably the nucleation process and, in this way, improves the kinetics of hydrogen absorption and enhances the absorption capacity of the composite. On the other hand, electron microprobe studies of the composite surface reveals the presence of V and Ti clusters along with some nickel agglomerates, indicating that the synthesis reaction of Mg_2Ni has not proceeded to completion (Fig. 5). The d-metal clusters presence is directly associated with the chemisorption of hydrogen and hence, with facilitation of the hydriding. A similar effect has been observed by the authors during previous investigations on magnesium-based composites containing $Mg_2Ni_{1-x}Fe_x$ [21] and $Mg_2Ni_{1-x}Co_x$ [22].

The kinetic curve of dehydriding at $T = 573$ K and $P = 0.15$ MPa of the composite 85 wt.% Mg_2Ni–10 wt.% V–5 wt.% Ti is presented in Fig. 6. For the sake of comparison the same figure shows the corresponding curve for a 90 wt.% Mg_2Ni–10 wt.% V composite as presented in a previous paper [19]. It is evident that the addition of a second metal and the increase of the total 3d-metal content in the

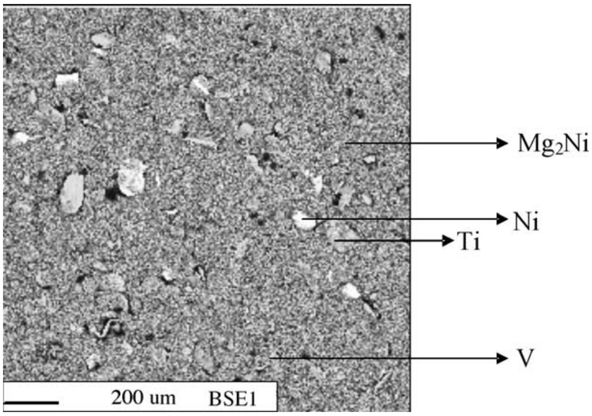

Fig. 5. Backscattering electron microphotograph of the composite 85 wt.% Mg_2Ni–10 wt.% V–5 wt.% Ti before hydriding.

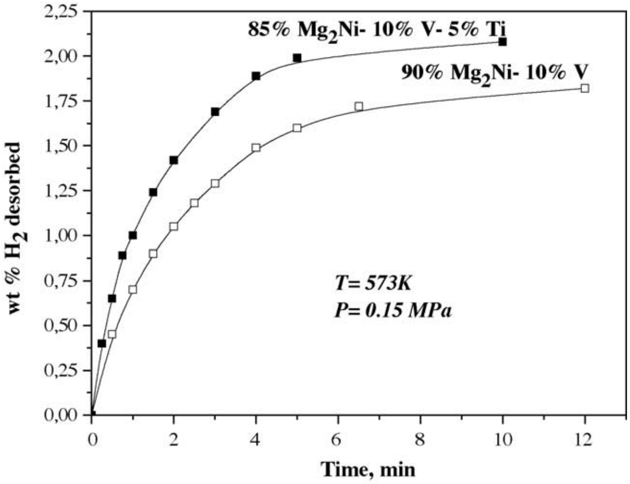

Fig. 6. Kinetic curves of dehydriding at 573 K and $P = 0.15$ MPa of: (■) 85 wt.% Mg_2Ni–10 wt.% V–5 wt.% Ti; (□) 90 wt.% Mg_2Ni–10 wt.% V.

composite contributes to improvement of its hydrogen desorption characteristics. A plausible explanation of this effect is the increase of the gas/solid interface as a result of formation of three hydrides: Mg_2NiH_4, $VH_{0.8}$ and $TiH_{1.92}$, which contributes to facilitation of the back diffusion of hydrogen.

4. Conclusion

The results obtained in the present study confirm previous experimental data, showing that addition of hydride-forming 3d-metals can improve the hydriding–dehydriding characteristics of Mg_2Ni. This effect, observed for the first time with the nanocomposites Mg_2Ni–V, is much more pronounced if titanium is added as a second 3d-metal to the composite. The effect mentioned consists in (i) improvement of the hydriding kinetics at temperatures below 573 K, (ii) enhancement of the hydrogen absorption capacity at 373–573 K, a non-negligible value of this capacity being observed during hydriding at room temperature, and (iii) improvement of the hydrogen desorption characteristics due to an increase of the gas/solid interface as a result of formation of 3d-metal hydrides along with Mg_2NiH_4.

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